STUDIES ON SOIL COLLOID PESTICIDE INTERACTIONS

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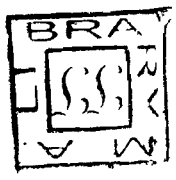

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This is to certify that the thesis entitled "Studies on soil colloid pesticide interactions" is the original work of Mr.Girraj Kishore Gupta and is suitable for submission for the degree of Doctor of Philosophy in Chemistry.

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A C K N O W L E D G E M E N T

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S. K. Gupta

(GIRRAJ KISHORE GUPTA)

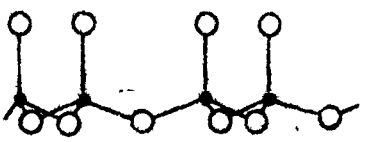
C O N T E N T S

GENERAL INTRODUCTION

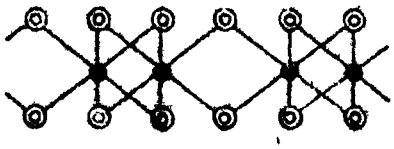
GENERAL INTRODUCTION

Investigations on the physico-chemical behaviour of clays and soils are of great theoretical and practical importance in the fields of agriculture, industry and technology. Soil material may be defined as the material occupying the outermost of the earth's crust and possessing distinct morphological, mineralogical, chemical and physical properties resulting from certain inheritance factors, from its unique position on the surface of earth, and from the environmental factors existing at that position. The word "physical" is inserted to distinguish it from purely logical systems, and the term corresponds with Joffe's[1] statement that the soil is a natural body.

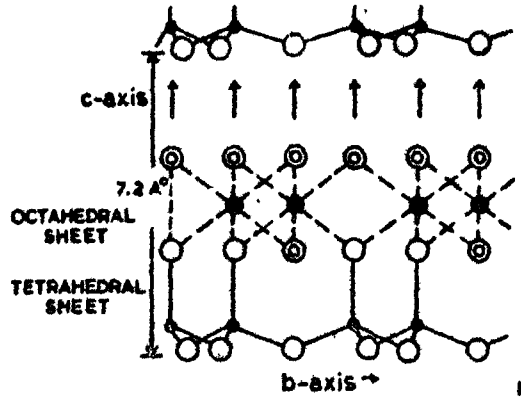
Extensive studies of x-ray diffraction patterns[2,3] have revealed that clay is crystalline in nature and composed of comparatively few and simple building units. The structures of common clay minerals have been determined in considerable detail by a large number of investigators based on the generalisations of Pauling[4]. Two structural units are involved in the atomic lattices of most of the clay minerals. The first is a silicon tetrahedron and the second unit consists of two sheets of closely packed oxygen or hydroxyls in which Al, Fe or Mg atoms are embedded in octahedral coordination. Combination of these structural units gives rise to the structure of the clay minerals that are found in the colloid clay fractions of soils (vide Fig.1).



TETRAHEDRAL SILICON SHEET



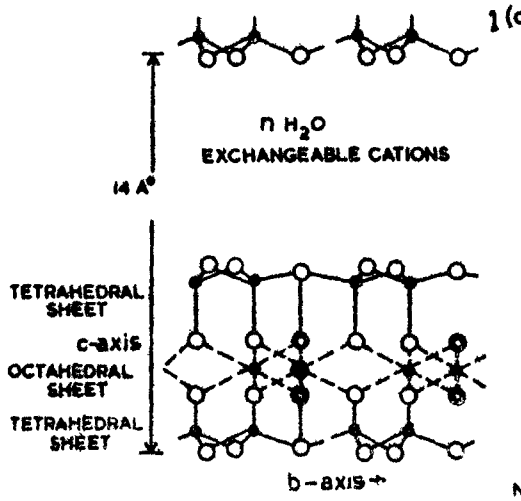
OCTAHEDRAL GIBBSITE SHEET



HYDROGEN BONDING	
4 (OH)	− 4
4 Al	+12
4 O+2 (OH)	−10
4 Si	+16
6 O	−12
NET CHARGE	0

1(a) KAOLINITE, A 1:1 LAYER SILICATE MINERAL

1(c) ILLITE STRUCTURE IS SIMILAR TO 1(b) EXCEPT THAT THE ELECTRICAL IMBALANCE IS SET RIGHT BY THE PRESENCE OF K IONS SITUATED BETWEEN ADJACENT LAYERS SO THAT THE NET CHARGE IS O.



6 O	−12
4 (Si, Al)	+16 or less
4 O+2 (OH)	−10
4 (Al, Fe, Mg)	+12 or less
4 O+2 (OH)	−10
4 Si	+16
6 O	−12
NET CHARGE	O or less e.g.-1

1(b) MONTMORILLONITE, A FREELY EXPANSIBLE 2:1 LAYER MINERAL. THE INTER-LAYER CATIONS ARE FREELY EXCHANGEABLE.

FIG. 1

KAOLINITE

Kaolinite is a hydrous aluminium silicate of approximate composition $Al_2O_3.2SiO_2.2H_2O$. The structure of this mineral was suggested by Pauling[4] and further work on the structure rapidly followed by Gruner[5]. Kaolinite, nacrite, halloysite and dickite are the isomers of the kaolin group. Dickite is the best crystallized member of the kaolin group. Relatively less work has been done on nacrite and dickite. In kaolinite the six dimension of the unit cell is about 8.93 A°. In presence of an interleaved layer of water it is supposed that the $(OH)_3$ layer of the kaolinite unit is no longer able to maintain its stretched condition and tends to revert to 8.62 A°. The exchange capacity of kaolinite mineral varies from 3 to 15 meq per 100 g.

MONTMORILLONITE

Le Chatelier[6] studied the material montmorillonites and presented the formula $4\ SiO_2.Al_2O_3.nH_2O$ for montmorillonite; this was accepted by Dana[7]. The clays of the montmorillonite group known as smectites, montmorillonoids and montmorins form a series with a wide range of chemical composition. This group includes nontronite, hectorite, saponite, pyrophyllite etc. They are all characterised by variable (001) spacing which accommodates more than two layers of water molecules with no clearly defined upper limit. Spacing as high as 30 A° have been recorded. X-ray studies have shown stacking of silica-alumina-silica units in the c direction, layers being continuous in direction a and b with the result that there exists a weak bond between them and an excellent cleavage. Water and

ether polar molecules can easily penetrate between the unit layers causing the lattice to expand in c direction. The c-axis dimension is, therefore, not fixed but varies from 9.6 Å to substantially complete separation of the individual layers in some cases.

Marshall and Hendricks[8,9] showed that montmorillonite always differed from its theoretical formula $(OH)_4Si_8Al_4O_{20}.nH_2O$, ($SiO_2$ 66.7%, Al_2O_3 28.3%, H_2O 5%) because of substitution within the lattice of Al, Mg, Fe, Zn, Cr etc., and of Si by Al or P, giving a series of group minerals. The b.e.c. of these clays varies between 80 to 150 meq/100 g. The simplest member of montmorillonite group is pyrophyllite $Si_2O_5Al_2O_4(OH)_2$-Si_2O_5. The complete layers are not chemically bound by electrostatic valencies but only by relatively weak van der Waals forces. Thus, in addition to the prominent basal cleavage, there is softness and flexibility caused by ready sliding of successive layers one over another.

ILLITE

The illite group[10], is relatively close to muscovite in chemical composition. The name illite was proposed as a family or group name. In illite group the degree of hydration is relatively low, and the characteristic basal spacing of muscovite at 10.1 Å is strong, although it may be broadened appreciably. The basic structure of illite species is very similar to that of montmorillonite with the difference that some of Si (+4) is replaced by Al (+3) and the resultant charge deficiency is balanced by K ions between the silica sheets of two successive units. In fact the

K ions act as bridges binding the unit layers so that they do not expand in presence of water.

The structural formula of the mineral is given as $(OH)_4Ky(Al_4Fe_4Mg_4Mg_6)\ (Si_{8-y}Al\ )\ O_{20}$. The size of the unit cell is 10 A°. The b.e.c. of these clays is much lower than those of montmorillonite species but higher than those of the kaolinite species and varies between 10 to 40 meq/100 g.

It has been reported[11] that K ions present in illites can be divided into three categories; K ions at surface exchange sites i.e., the outer planar surfaces of the clay minerals, K ions in interlattice positions near the edges of the clay particles, and K ions in interlattice positions away from the edges. These potassium ions are replaceable from all these positions but the rate and ease of exchange varies, those at the outer planar surfaces being most rapidly replaceable by all cations.

PHYSICO-CHEMICAL PROPERTIES OF CLAY MINERALS

The clay particles, by virtue of their very structure, often pass over to the colloidal state when brought in contact with water. The ultimate clay particles appear to exist in the form of a very complex anion, exposing a highly negative surface, comparable to the inner part of the double layer, the outer layer being made up of a swarm of rather loosely held cations surrounding the particle. When such particles are dispersed in water the cations gets hydrated and then dissociate to a certain distance from the surface, finally leading to the formation of a diffused electrical layer[12]. In

other words, a suspended clay particle may be compared to a dissociated electrolyte, the size of its ions falling within colloidal range.

Clay suspensions can be considered intermediate between lyophobic and lyophilic colloids. In view of the importance of physico-chemical properties like electrometric behaviour at reversible electrodes, ionic adsorption and exchange, thermodynamic equilibrium, zeta potential, viscosity, thixotropy and clay organic interactions when investigating clay minerals and soils, a critical study of these properties can provide results of great significance in the case of these colloids.

The results on the titrations of clay suspensions with bases reveal that the pH variations are in a manner comparable to those of weak acids. The work of Mukherjee[13,14,15] and co-workers, Bradfield[16] and others bear enough testimony to this fact. A more critical survey of their weakly acidic character had led to a better understanding of the nature of clays. It appears that the soil is an electrochemical, or polar system, having a dominant acid character, and that the H-clay is the extreme acid form of its inorganic adsorption complex. Weigner[17] was the first to recognise the important part played by electrical double layer in the interaction of H-clays with acids, bases and salts. According to him, the acidic character of hydrogen clays is due to the swarm of H^+ ions present in the electrical double layers surrounding the H-clay particles. Acidic clays also contain exchangeable Al, which being trivalent, is very lightly bound to the clay surface.

Different ideas have been put forward to account for the acidic character of clays. According to a number of workers clay acid is not an Arrhenius acid having ionizable H^+ (and or Al^{3+}) ions. It is more like a Lewis acid. According to Goates[18] et al., the Arrhenius acid character functions below pH-7, and the Lewis acid behaviour is evident at higher pH values.

Electro-chemical methods have found extensive use in studying the physico-chemical properties of soils. Many authors including Mukherjee[19,20], Mitra[21,22], Marshall[23], Brindley[24], Puri[25], Grim[26], Goates[18], Low[27], Adhikari[28] and Chakravarti[29] have carried out an extensive and critical study of the various electro-chemical aspects of ion exchange in clays and related materials, using potentiometric and conductometric methods. These methods have proved valuable in throwing light on the mechanism of clay-organic interactions. It is proposed to utilise electrometric studies for the investigation of the reaction mechanism between pesticides and some standard clays.

ADSORPTION

The surface of a liquid is in a state of strain, or unsaturation, and that of a solid has, similarly a residual field of force; there will consequently be a tendency for the free energy of any surface to decrease, and it is this tendency which is ultimately responsible for the phenomenon of adsorption.

The term adsorption as applied to the condensation of molecules on the surface of solids may involve two or less distinct type of phenomena. In the first adsorption type, the surface

condensation is due to physical capillary phenomena, more or less non-specific, in that the adsorption parallels the physical character of the adsorbent. Physical adsorption is of reversible type and a low temperature adsorption. It has been reported to by different authors as "physical", secondary "reversible" and "van der Waals" adsorption. The second type of adsorption, which appears to be due to primary valance forces, is relatively strong and specific, being largely independent of the physical character of the adsorbent, in other words, the adsorption is essentially of chemical nature. The chemical or activated adsorption is non-reversible and is high temperature adsorption. The study of the adsorption is important in understanding the mechanism of interaction of simple organic molecules and pesticides on soils and clays.

Chemically soils are alumino silicate systems and as such are characterised by possessing exposed surface being rich in oxygen atoms and hydroxyl groups. These surfaces are basically highly polar in character and possess an intense residual force. Generally these forces are responsible for holding the other ions or molecules at the surface temporarily or permanently depending on the forces operating at it. Residual valance forces, dipolar attractions or any other physical forces of the van der Waals type lead to adsorption, where the molecules are held temporarily, while chemical or electrostatic forces give rise to a permanent binding and molecules stay permanently on the surface.

The clay minerals provide interesting material for the

study of adsorption phenomenon. The clay minerals predominantly exhibit exchange adsorption. Exchange reaction with inorganic cation is stoichiometric and is of fundamental and practical importance in all the fields in which clay minerals are used and studied. In adsorption, cation exchange reaction occurs with possible van der Waals interactions. Often strongly cation dipole attractive forces play an important role in adsorption of polar molecules on layer silicates. Solvation of the cations by the polar molecules has been observed and complex formation takes place through cation dipole interactions. The oxygens of the clay surface which are negatively charged, also act as bases, competing with the organic base for the protons of water molecules.

It appears that chemical adsorption by montmorillonite can occur in three different manners (i) protonation at the silicate surface, by reactions of base with hydronium ion on the exchange site; (ii) protonation in the solution phases with subsequent adsorption of organic molecule via ion exchange; and (iii) in systems having low water content, protonation by reaction with dissociated protons from the residual water present on the surface or that in coordination state with the exchangeable cations.

Studies in these fields can be a source of attractive information and can provide useful data for studying the many reactions that occur in soil, improve our understanding of the soil pesticide relationships, as well as, the role of fixation and release in plant nutrition.

ADSORPTION ISOTHERMS

Adsorption isotherms can be used to provide information on the mechanism of interaction of compounds with soil and clays. Equations which express, at a constant temperature, the relations between the amount of a substance adsorbed (x) and the concentration (c) are known as adsorption isotherms. A model for the adsorption process was first presented by Freundlich in form of the equation

$$x = kc^n, \text{ where } n < 1$$

This expression lacked a theoretical basis and failed if the concentration of the adsorbate was too high.

A more significant isotherm was that of Langmuir[30] which was originally derived in 1916 by a simple theory for the case of physical adsorption of a gas on a plane solid surface assuming unimolecular thickness. This isotherm for the process of chemisorption was of the form

$$\frac{c}{x/m} = \frac{1}{Kb} + \frac{c}{b}, \text{ where K and b were the constants.}$$

Neither the Freundlich nor the Langmuir equation was capable of representing the S Shaped (Sigmoid) isotherms which were obtained when the adsorption of vapours on a porous solid was studied at high vapour pressures. The B.E.T. equttion was then derived for multimolecular adsorption. The equation represented fairly satisfactorily the adsorption of water by textiles, silica gel etc. It was first applied to soil systems by Nelson and Hendricks.

Preferential or selective adsorption of second component was also found possible and an equation for composite isotherm was proposed. In general composite isotherms showed a smooth variation with composition of solution. In some cases, however, steps and sharp discontinuities were observed. These were attributed to the appearance of a second layer of adsorbate on the top of the first[31] or due to a phase change in adsorbate. Sharp breaks in the isotherms were also due to the change in orientation of the adsorbate. Venturello[32,33] published a series of papers in which he presented such isotherms for adsorption by inorganic solids, alumina and silica gel, from solutions of dye stuffs in water and of iodine in organic solvents. It was suggested that different parts of the isotherms corresponded to adsorption on sites of differing energy due to heterogeneity in the surface.

A classification of the different isotherms obtained during adsorption was proposed by Giles[34] et al. The Langmuir type curve was obtained when there was no strong competition from the solvent for sites on the surface and the adsorbate had linear or planar molecules. A 'S' shaped curve was obtained if the solvent was strongly adsorbed, there being a strong intermolecular attraction within the adsorbed layer and the adsorbate was monofunctional. An 'H' shape occurred when there was high affinity between the adsorbate and adsorbent as in very dilute solutions during chemisorption or during adsorption of polymer or ionic micelles. A 'C' type of curve was obtained when there was constant partition of the adsorbate between the solution and adsorbent as in textile fibres. A less common shape involved was a wave. The change in

slope occurred at a small value of adsorption and indicated a form of co-operative[35] adsorption, with some degree of deformation packing in crystalline state. The homogeneous surface adsorbed one component of a binary mixture more strongly than the other; this resulted in a 'U' shaped composite isotherm.

Plateaus and maximas were observed in adsorption isotherms. A long plateau in the adsorption isotherm indicated saturation of a surface and the fact that a high energy barrier had to be overcome before additional adsorption could occur on new sites. It is proposed to study the phenomenon of adsorption of certain pesticides on clays with the help of adsorption isotherms.

CATION EXCHANGE IN CLAYS

Properties which affect cation exchange reactions in clays can be listed as follows: (1) Structural characteristics; (2) Charge density and distribution. The size, shape and charge distribution of clay minerals determine , in a large measure, any special affinity which ions have for various types of clays. A number of experiments on the relationship between the clay structure and adsorption of ions K^+, NH_4^+, Rb^+ and Cs^+ have shown rather conclusively that the sizes of these ions are such that they fit quite strongly into the void formed by oxygen rings in the Si-O layers of the three-layers clays. In addition, this holding is favoured by isomorphous substitution in the Si-O layer and a high charge density seems to be important[36,37,38].

Valence has a profound effect on the affinity of ions for clays. Hendricks[39] showed mathematically that trivalent and divalent ions normally have an advantage over monovalent ions. Despite the general trend of increasing affinity with increasing valence, Coleman and his students[40] found that, at high concentration, K^+ is a better competitor than either Ca^{2+} or Al^{3+} for exchange spots on clays. The reason for this is not at hand, but it may possibly be related to the high configurational entropy of an exchanger with di- or trivalent ions[41] which arises because of the many different ways in which polyvalent ions can be arranged on the exchange sites. Marshall[42] postulated that clays formed under the influence of divalent cations (Ca^{2+} and Mg^{2+}) possess exchange spots arranged in pairs, which would help to account for the high affinity montmorillonite has for alkaline earth metals. The fact that montmorillonite tends to hold Ca^{2+} quite strongly, compared to K^+, whereas the tendency is reversed in kaolinite has also been ascribed to a 'Donor' effect by Wickland[43] and others.

Ion exchange is inherently a stoichiometric process. Any counter ions which leave the ion exchanger are replaced by an equivalent amount of other counter ions. This is a consequence of the electroneutrality requirement. When a counter ion moves out into the solution, the ion exchanger is left with an electric surplus charge which it must compensate by taking up another counter ion. The total counter ion content thus remains constant, irrespective of ionic composition.

The stoichiometry of ion exchange requires that the fluxes

of the two exchanging counter ions be equal in magnitude, even though the counter-ion mobilities may by quite different. It is important to grasp the mechanism which brings about this equivalence of fluxes. The faster ion, of course, tends to diffuse at the higher rate. However, any excess flux of an ion is equivalent to a net transfer of electric charge and thus produces an electric field which slows down the faster ion and accelerates the slower ion so that the fluxes become equal. The fluxes of the two counter ions are electrically coupled in exactly the same way as the fluxes of the cation and anion in electrolyte diffusion in free solution.

The size of the clay particles and the position of the exchangeable ions are of great importance to the speed of attaining equilibrium. The differences between clays in which exchange takes place inside thin intersheet spaces as opposed to surface exchange would be thought to be very great. Unfortunately, only a small amount of work was done by the early workers[44] before information was available on the mineralogy of the clays used. One can, however, learn a great deal about the principal factors influencing the speed of exchange by studying the work done on resinous exchangers[45,46].

The interactions of particular cations (e.g., K^+ and Al^{3+}) with clays not only may affect the speed of reaction, but also influence the equilibrium which is obtained. The fact that many cation exchange reactions attain different equilibria depending on the side from which the equilibrium is approached has been known for long time[44]. This phenomenon, called hysteresis

obviously is a reflection of changes in the clay adsorbing surface, changes which are brought about by cation clay interactions. Examples of effects which produce hysteresis are collapse of vermiculite upon K^+ or NH_4^+ saturation[37] and the fixation of polymeric hydroxyl Al in a form not replaceable by neutral salts.

Ion exchange equilibrium can be characterized by the ion exchange isotherms. These isotherms are a graphical representation which, in principle, cover all possible experimental conditions at a given temperature. Equilibrium can also be described in terms of a quantity such as the separation factor, selectivity coefficient or distribution coefficient. As a rule, these quantities vary with experimental conditions. Thus, any specific value of one of these quantities corresponds to only one point on the isotherm surface.

Ion exchange isotherm shows the ionic composition of the ion-exchanger as a function of the experimental conditions. Various ways of representation can be used. As a rule, the equivalent ionic fraction, $\bar{X}_A$, of the counter ion A in the ion-exchanger is plotted as a function of the equivalent ionic fraction X_A in the solution, while the other variables are kept constant. In a hypothetical system, the ion exchange isotherm may be linear but ion-exchangers in general select one counter ion in preference to another. Selectivity thus necessitates a non linear isotherm.

The preference of the ion-exchanger for one of the two counter ions is often expressed by the separation factor. This quantity is particularly convenient for practical applications.

The separation factor is the quotient of the concentration ratios of the two counter ions in the ion-exchanger and the solution. If the ion A is preferred, the factor α^{A}_{B} is larger than unity, and if B is preferred, the factor is smaller than unity. The numerical value of the separation factor is not affected by the choice of the concentration units.

Sometimes instead of the separation factor, the selectivity coefficient can be used for describing ion-exchange equilibria. Molarities or equivalent ionic fractions can be used instead of molalities when we get the molar and rational selectivity coefficients respectively. For counter ions of equal valence, the numerical value of the molal, the molar, and the rational selectivity coefficients are identical and are related to the separation factor by

$$K^{A}_{B} = K'^{A}_{B} = {}^{N}K^{A}_{B} = (\alpha^{A}_{B})^{|z_A|} \qquad (z_A = z_B)$$

where K'^{A}_{B} and ${}^{N}K^{A}_{B}$ are the molar and rational selectivity coefficients, respectively. For counter ions of different valences, the numerical value of the selectivity coefficient depends on the choice of the concentration scale. The essential difference between the separation factor and the selectivity coefficient is that the later contains the ionic valences as exponents. Thus, the separation factor is usually quite different from the selectivity coefficient, if the valences of the competing counter ions are not equal.

In certain practical applications, equilibrium is most conveniently expressed in terms of the distribution coefficients of the counter ions. The distribution coefficient is defined as the

number of milliequivalents of an ion adsorbed per gram of exchanger divided by the number of milliequivalents of that ion per ml remaining in solution at equilibrium and is, therefore, a direct measure of the extent to which an ion is removed from solution when the exchanger is added. The coefficients increase with dilution of the solution. For any given conditions, the distribution coefficients can be calculated from the selectivity coefficient.

In theoretical studies, the thermodynamic equilibrium constant is occasionally used. This quantity is defined by the thermodynamic relationship:

$$\Delta G^{\circ} = - RT \ln K_{B}^{A}$$

The equilibrium constant is an integral quantity characteristic of the whole isotherm surface and is a true constant depending on temperature only. The equilibrium constant gives no information about the exact counter ion distribution under any particular experimental conditions. The nature of the equilibrium constant obtained depends on the choice of the standard and reference states and thus it can be molal or rational equilibrium constant. Studies on ion-exchange equilibria in homoionic clays provide extremely useful results, and would be undertaken in these investigations.

THERMODYNAMICS OF EXCHANGE

The various changes and transformations which occur in nature are accompanied by energy change. Thermodynamics is the exact mathematical science that describes the interrelationship

of heat and mechanical energy. It is concerned with the chemical and physical processes which involve the conversion of one form of energy into another. It describes transformation of matter and energy when the atomic constitution of matter can be ignored. Chemical thermodynamics deals with the study of processes in which chemical energy is involved. It can indicate whether a particular reaction is feasible or not under a given set of conditions of temperature, pressure and concentration. Thermodynamics, therefore, is a fundamental subject of great importance.

FREE ENERGY CHANGES

This function provides the true measure of chemical affinity under conditions of constant temperature and pressure. This free-energy function has been found to have the very useful property of predicting the maximum yields obtainable in equilibrium reactions. The free energy change in a chemical reaction can be defined as $\Delta G = G$ (products) - G (reactants). When the free energy is zero, the system is in a state of equilibrium. When the free energy change is positive for a proposed reaction, net work must be put into the system to affect the reaction, otherwise it cannot take place. When the free energy change is negative- the reaction can proceed spontaneously with accomplishment of net work. For this reason ΔG has often been called the driving force of the reaction. While free energy change during a reversible process (i.e., when the system is in the equilibrium) is zero, the free energy change during an irreversible or spontaneous process, has a negative value. While free energy decreases in all spontaneous processes, it remains

unchanged in reversible processes carried out at constant pressure and temperature. This driving force depends upon the concentration of the reactants and products. It also depends on their specific chemical constitution, and on the temperature and pressure, which determine the molar free energies of reactants and products. This quantity is, thus, of great importance.

ENTHALPY CHANGES

Enthalpy may be defined as the heat content or total energy stored in a system. It is defined by the equation:

$$H = E + PV ,$$

where E is the internal energy of the substance.

The symbol ΔH is used to express the change in enthalpy (or heat content) of a system accompanying a change in state, such as a chemical reaction. A positive value of ΔH means that heat is absorbed from the surroundings and the reaction is endothermic. A negative enthalpy change indicates an exothermic reaction. It is indicative of the strength or tightness with which an ion is held on a surface.

The change in enthalpy of a system can be calculated from a knowledge of free energy changes. Thus using the Gibbs-Helmholtz equation and the van't Hoff isochore, the standard enthalpy changes ΔH°, can be calculated. Enthalpies of reaction can also be determined by the use of instruments such as the Bomb calorimeter.

ENTROPY CHANGES

The concept of entropy was introduced about 1850 as a thermodynamic quantity in the analysis of the efficiency of heat energies. Thirty years later Boltzmann suggested that this thermodynamic quantity could be defined by the expression:

$$S = K \ln W$$

From the above equation we see that an increase in W results in an increase in S. Thus a spontaneous change in macro state of an isolated system is always accompanied by an increase in entropy. The change of entropy of a system may be defined as the integral of all the terms involving heat absorbed (Q) divided by the absolute temperature (T) during each infinitesimally small change of the process carried out reversibly. The entropy is expressed in calories per degree. Since a pure crystalline substance at $0^{\circ}K$ consists of stationary ions, atoms, or molecules perfectly arranged in the crystal lattice, its entropy is zero. At temperature greater than $0^{\circ}K$ the unit in crystal lattice vibrate about a fixed position, thus giving rise to an increase in entropy. The systems becomes more and more disordered as the temperature increases leading to still further increase in entropy. A negative entropy indicates lesser randomness of motion, an increase in stability or rigidity of the system with less in degrees of freedom of the reactants in the product formed as a result of reactions like fixation, adsorption, immobilisation etc. Since all natural processes are proceeding spontaneously, i.e., irreversibly, the

entropy of universe is increasing continuously. According to Clausius the energy of the universe is constant, the entropy of the universe tends towards a maximum.

A knowledge of thermodynamics and the various functions can be very useful in chemical interactions and studies on clay-organic interactions can be usefully undertaken with their help.

KINETICS OF EXCHANGE

Chemical kinetics deals with the measurement of rate of reactions under specified conditions of temperature, pressure and concentration. It has proved a highly useful science. Kirchhoff[47] was the first to apply this science to rate of homogeneous reactions. The rate of a homogeneous reaction may be represented by the equation

$$R = k\,(A)^{x}\,(B)^{y}$$

The ion exchange process is, however, quite different from such simple chemical reactions. It is concerned with a reaction which involves transport of ions from solution into exchanger and vice versa. It is, therefore, heterogeneous. For dilute solutions, there is effectively no electrolyte penetration into the exchanger and hence the co-ion has no part to play in the overall reaction mechanism:

$$X^{-}A_{soln}^{+} + (B^{+}\text{-}R^{-}) \longrightarrow X^{-}B_{soln}^{+} + (A^{+}\text{-}R^{-})$$

The first serious attempt to elucidate the rate-controlling mechanism in ion exchange processes was made by Nachod and Wood[48].

They concluded that the rate determining step in the case of sulfonated coal was film diffusion.

Kunin and Myers[49] studied the kinetics of anion exchange using a number of anion pairs and concluded that particle diffusion was the rate-controlling process.

A great advancement in this field was made by Boyd, Adamson and Myers[46]. Although in chemical processes, film diffusion and particle diffusion had previously all been separately postulated as possible rate-determining mechanisms, they gave for the first time a clear analyses of the kinetics corresponding to each hypothesis. They investigated the kinetics of exchange of several ion-pairs with phenol sulphonated resins and concluded that at low concentrations in solution of the displaced ion, film diffusion was rate controlling while for higher concentrations particle diffusion was rate controlling.

There are, thus, three distinct kinetic processes in ion exchange reactions:

1. Film diffusion in the unstirred layer of solution close to the exchanger particle.
2. Particle diffusion of ions in the matrix.
3. Chemical exchange reaction.

Of all the exchange kinetics which have appeared in the literature to date, none have been shown to be controlled by the chemical exchange step.

PARTICLE DIFFUSION

In particle diffusion the rate of exchange is characterised by an initially rapid step followed by progressively slower rates as the exchange proceeds. When a sample of exchanger in the i-form is placed in a well-stirred solution of large volume (infinite bath conditions) initially devoid of isotope i, the rate of the exchange reaction is given by the equation[50]

$$U_{(t)} = \left[1-\exp\ (\bar{D}t^2/r_o^2)\right]^{\frac{1}{2}} ,$$

where $U_{(t)}$ is the fractional attainment of equilibrium. The half time of the exchange, $t_{\frac{1}{2}}$, may be obtained by substituting $U_{(t)} = 0.5$ in the above equation so that

$$t_{\frac{1}{2}} = 0.030\ r_o^2/\bar{D}$$

A plot of $U_{(t)}$ versus t is characterised by a very rapid initial exchange followed by subsequent falling off as concentration gradient diminishes within the exchanger.

FILM DIFFUSION

When the slow step is diffusion across the unstirred solution layer at the surface of the exchanger, film diffusion controls the rate of exchange. Concentration gradients occur only in the solution phase. For infinite bath conditions, in which isotope i remains essentially zero in the bulk solution throughout the exchange, the expression for fractional attainment of equilibrium becomes[50],

$$U_{(t)} = 1-\exp\ (-3\bar{D}Ct/r_o\ \delta\ \bar{C})$$

The half time of reaction, $t_{\frac{1}{2}}$, is obtained by substitution of $U_{(t)} = 0.5$ so that

$$t_{\frac{1}{2}} = 0.23\, r_o \delta \bar{C}/DC$$

The interruption test[51] is the best technique for distinguishing between particle and film diffusion control. The nature of the rate-determining step can also be predicted by use of the simple criterion[51]:

$$\frac{\bar{X}D\,\delta}{CDr_o}\left(5 + 2\alpha\frac{A}{B}\right) = \phi \gtrless 1$$

ACTIVATION ENERGY

The activation energy of a reaction is defined as the additional energy which the reactant molecules must acquire in order to form the activated complex for the reaction. It is the difference in energy of the activated complex and the reactants.

Increase of temperature increases the rate of a chemical reaction to a great extent. The most satisfactory method for expressing the influence of temperature on reaction velocity can be derived by plotting log k against 1/T. An exponential form of this equation has been given by Arrhenius:

$$k = Ae^{-E/RT} ,$$

where E is the energy of activation and A is the frequency factor. The Arrhenius equation in terms of diffusion coefficients can be written as[52]

$$D^i = D^i_o \exp(-E/RT)$$

The energy of activation can be evaluated from the above expressions and also from specific rates k_1 and k_2 for two temperatures T_1 and T_2 from the equation[53]

$$\log \frac{k_2}{k_1} = \frac{E}{2.303R}\left(\frac{T_2-T_1}{T_1\ T_2}\right)$$

The rate of a chemical reaction is related to the activation energy. The greater the activation energy the slower the reaction.

OTHER THERMODYNAMIC FUNCTIONS OF ACTIVATED STATES

The standard free energy ΔG_a, entropy ΔS_a and heat of activation ΔH_a respectively are the quantities that represent the difference between the values of the respective thermodynamic functions for the activated complex and the reactants. Because of the transient nature of the activated complex, there is no hope of being able to determine these thermodynamic properties by direct measurement.

The specific rate of a reaction, at a given temperature, is determined by ΔG_a, the free energy of activation. Higher the value of ΔG_a in a reaction, the slower is the rate of the reaction at a given temperature. ΔH_a shows that the lesser the value of ΔH_a faster the reaction. Entropy of activation, ΔS_a is related with randomness of the reaction. If the formation of the transition state requires the imposition of a high degree of organisation in the way the reactant molecules much approach each other, and also of the concentration of their energy in particular linkages so as to allow to their ultimate breakage, then the attainment of transition

state is attended by a sizeable decrease in entropy or randomness, that is, a negative value of entropy points to a slow exchange reaction.

X-RAY DIFFRACTION

X-ray studies have played a vital role in clay mineral researches as reported by Brindley[54], Buerger[55], Bragg[56] and others. They have proved valuable in investigating the mechanism of adsorption of organic compounds on clays. Thus mono or multimolecular adsorption has been studied. Planar and edge complexes have been investigated and orientation[57] studies carried out from the basal thickness observed by x-rays. It is proposed to examine clay-organic reactions with the help of x-ray diffraction.

INFRARED SPECTROSCOPY

Infrared studies on clays have been directed towards characterising the types of clay mineral that occur naturally in soils, and to obtaining information on the surface properties and reactivity of these minerals. Infrared spectroscopy has also given an exceptional insight into the mechanism of adsorption phenomena. The adsorptive forces modify the vibration of adsorbed molecules, or new molecular species may be formed, as when bases are converted to their protonated cation, so that several types of adsorption can be distinguished in a single system; sometimes the sites of adsorption can be identified by the perturbations of the vibrations of the adsorbent.

Infrared with the oriented films can permit the orientation

of adsorbed molecules relative to the silicate layers to be determined. Work has been concentrated on montmorillonite, and for this mineral a fairly full picture of adsorption mechanism is now available. Three different mechanisms have been well established by infrared spectroscopy for the adsorption of polar molecules on layer silicates; all involve the exchangeable cations. These are (a) direct coordination to the cation, (b) indirect coordination through a bridging water molecule, and (c) conversion of adsorbed bases to the protonated cation.

In view of the importance of infrared spectroscopy in investigating the mechanism of reactions, it is proposed to utilize this technique for the studies on the mechanism of adsorption of pesticides on clays.

PESTICIDES

In man's continuous fight[58] against his insect enemies, chemical treatment has come to play the most important role. At present a large number of organic chemicals are in commercial use for insecticidal action. These pesticides may be broadly grouped into inorganic and organic. Further division can be into anionic, cationic and non-ionic. The generally used inorganic pesticides are lead arsenate, calcium arsenate, paris green, nickel chloride, cuprous-oxide, mercuric chloride, mercurous chloride and zinc phosphide. Organic pesticides commonly used are aldrin, B.H.C., D.D.T., 2,4-D, lindane, nicotine and its compounds, D-D mixture, telone, nemagon, s-triazines, chlordane, dieldrin, parathion, malathion, amitrol, zineb and ziram.

The above pesticides are used as insecticides for the control of harmful insects, as herbicides for destroying the weeds and other unwanted vegetation, as fungicides for the control of plant fungi, as acaricides for the control of mites and as the nematocides for the control of nematodes and round worms. Their widespread use makes it desirable to know, as much as possible, concerning their behaviour after they are applied to the soil.

Among the pesticides nicotine is a volatile alkaloid. It was the earliest organic chemical to be used as a pesticide. The pure alkaloid was synthesized in 1904 by Pictet and Rotschy[59]. Nicotine, nicotine sulphate and various fixed nicotine compounds such as bentonite, tannates, humates, resinates etc., have been used as contact insecticides, as fumigants and stomach poisons. Deong[60] found that the toxicity of nicotine and nicotine sulphate to aphids, both as sprays and as fumigants increase with the pH of the solutions.

D-D mixture is a mixture mainly of 1,2 dichloropropane and 1,3 dichloropropene. It is used as a soil fumigant, especially for the control of root knot, eelworms, nematode and fungus diseases in soils. It is available in liquid form and is volatile.

Among zinc formulations ziram is the coined name of zinc dimethyl dithiocarbamate and zineb that of zinc ethylene bisdithiocarbamate. Both are widely used as protective sprays against a number of diseases of vegetables and ornamentals and against damping off of cotton seedlings. Some plants are able to

adsorb zinc from these pesticides and hence their use is of great importance in areas where zinc is deficient in the soil. Zinc phosphide is used as an inorganic pesticide. Zinc pesticides often leave zinc residues in soils as a result of degradation which then also serves as an important micronutrient.

CLAY PESTICIDE INTERACTIONS

The three classes of pesticides viz., cationic, anionic and non-ionic (polar), are generally applied as their aqueous salt solutions. Cationic pesticides, being completely ionized, are adsorbed by clays and soils through an ion-exchange process, replacing the inorganic cations initially present at the silicate surface. The anionic pesticides tend to be negatively adsorbed, that is, they are repelled from the negatively charged clay surface. At low pH, the acidic functional groups in these molecules may accept protons, giving rise to an uncharged species. In the pH range commonly encountered in soils, the non-ionic organic pesticides are taken up and retained by clays predominantly in molecular form. Their adsorption is therefore determined chiefly by ion dipole interactions. In acedic media these compounds may acquire a positive charge by accepting a proton and so behave as cations.

One of the early attempts to elucidate the mechanism underlying the clay pesticide interactions was due to Frissel whose findings and conclusion were subsequently summarized by Frissel and Bolt[61]. These workers studied the uptake from an aqueous environment of some 14 organic herbicides by montmorillonite,

illite and kaolinite as a function of pH and electrolyte concentration.

The reactions of amitrole with montmorillonite were studied by Russel et al.[62] The interaction between ethyl N, N-di-n-propylthiolcarbamate and montmorillonite saturated with different cations was reported by Mortland and Meggitt[63]. Negative adsorption of 2,4-D by sodium saturated montmorillonite and kaolinite at pH 6 was observed by Weber et al.[64] The interaction of diquat and paraquat with clay minerals was found to be one of ion exchange process replacing an equivalent amount of inorganic cations.

Hendricks[65] showed that purines and nucleosides were intercalated by hydrogen-montmorillonite through a proton transfer reaction and that the basal spacing of the complexes so formed was correlated with molecular configuration. He also demonstrated that brucine and codeine, being strong bases, were intercalated by hydrogen montmorillonite through proton transfer and physical adsorption. Nicotine, neutralized stoichiometric amounts of hydrogen ions held by various clay minerals[65], because the molecule occupies less than the equivalent area per exchange site. In the case of montmorillonite saturated with polyvalent cations protonation may occur due to the polarized water molecules in direct coordination with these cations.

Seven factors are known to influence the fate and behaviour of pesticides in soil systems. These are chemical decomposition, photochemical decomposition, microbial decomposition, volatilization, movement, plant or organism uptake and adsorption. The phenomenon

of adsorption-desorption directly or indirectly influences the magnitude of the effect of the other six factors. Adsorption, therefore, is one of the major factors affecting the interactions occurring between pesticides and soil colloids. It was shown that factors[66] such as soil or colloid type, physical-chemical nature of the pesticide, soil reaction, temperature, nature of the saturating cation on the colloid exchange sites, and the nature of the formulation directly influenced the adsorption-desorption of pesticides by soil systems. The role of some of these factors will be examined in the present studies.

SOIL ORGANIC MATTER

Soil organic matter is the most complex material present in soils. In addition to the organic constituents present in undecayed plant and animal tissues, soil organic matter contains living and dead microbial cells, microbially synthesized compounds, and materials produced as a result of microbial activity. The organic matter content of soils plays an important part in determining the qualities of a soil. Rich soils are distinguished by their high percentage of organic matter content. Organic matter helps to improve the physical properties of a soil like structure, water holding capacity and tilth. The soil is made spongy, aeration of the soil and sub-soil is facilitated, as also drainage. It also promotes greater biological activity in the soil leading to better nitrification and nitrogen fixation. Freshly decomposing organic matter is also a source of nitrogen supply for plants. In the studies reported in this thesis the effect of a nematocide on organic matter content of some Indian soils has been studied.

NITROGEN

Nitrogen is a vitally important nutrient element, the supply of which in the soil may be markedly influenced by man. Most of this nitrogen is held in tight chemical combination in soils and is released only very slowly through bacterial decomposition of soil organic matter. The combined mineral forms in which nitrogen is assimilated are the nitrate (NO_3^-) and the ammonium (NH_4^+) ions. Organic nitrogen is gradually depleted from the soil through oxidation and the activities of micro-organisms. The rate of this loss depends upon various factors of which soil texture, aeration, soil temperature, permeability and erosion are important ones. Repeated cultivation, as also cropping, reduces the nitrogen content in soils. It was considered that a study of the effects of an important nematocide on the nitrogen status of some Indian soils will be quite useful.

PHOSPHORUS

The phosphorus in the soil is present in two forms: organic and inorganic. Plants utilise phosphorus in the mineral form and hence the organic form has to be mineralised before this element is available. The inorganic forms of phosphorus occur usually as compounds of calcium or iron and aluminium phosphates. All these forms are highly insoluble and are rarely of much use to the plant. Since plants can absorb phosphorus only when it is present in a soluble or weakly held condition, the condition in which the phosphorus is present in the soil is a very important factor. Both acidic and alkaline reactions in soil restrict and reduce phosphate

availability and a pH range between 6.5 and 7.5 is ideal for phosphate availability. The importance of phosphorus in plant and animal nutrition is well recognised. It is present in seeds in larger amounts than in any other part of plants, although it is found extensively in the young growing plants. Sufficient quantities of phosphorus are necessary for normal transportation of carbohydrates in the plants, like conversion of starches into sugars. Also, they help in the assimilation of fats in plants. A study of the effects of pesticides on phosphorus status of soils is bound to be of great practical utility.

POTASSIUM

Potassium occurs in both soluble and insoluble forms in the mineral component of soils. A large proportion of soil potassium is in the primary minerals, like the micas and feldspars which occur in the sand and silt fractions. Most of the total potassium in a soil is in non-exchangeable form. Williams[67] suggested three categories of K^+ in soils viz., non-exchangeable, fixed and very slowly available. A part of the potassium gets 'fixed' in the clay minerals like illite, montmorillonite and vermiculite. Such fixed potassium becomes available again only gradually. Potassium is absorbed by plants as the K^+ ion. A good supply of potassium is essential if saline alkali soil is to be utilised. Toxicity of the sodium ion can be reduced by potassium due to an antagonistic ion effect. In sodium soils a high content of available or partially available potassium is important to maintain the sodium potassium balance and a well developed microflora will be important

in this respect[58]. On account of the role of potassium in soils it was considered worthwhile to examine the effect of an important fumigant on its availability in soils.

CALCIUM CARBONATE

Calcium carbonate occurs in the form of calcite in some crystalline rocks but it is more generally deposited as a secondary mineral from water. Lime containing complex silicates are weathered by carbon dioxide charged water to liberate soluble hydrogen carbonates which eventually reprecipitate as carbonates. Calcareous soils develop particularly in arid regions where carbonate is precipitated at various depth depending upon the effective depth of leaching. An excess of calcium carbonate can introduce too much calcium into the soil complex and can lead to deficiency of minor elements. Volatilisation of ammonia is correlated to calcium carbonate. On account of the role of calcium carbonate in soils it was considered necessary to study the effect of D-D mixture on this constituent.

THE PROBLEM

During the last few decades a variety of organic and inorganic chemicals have been used as pesticides and trace metals to increase food, fodder and fiber production. Their use while beneficial in several ways has brought its own problems. Without intelligent control there are dangers of environmental pollution and contamination on an every increasing scale. Researches have been carried out on regulated uses of pesticides in crop production.

It has been established that on application to soils the pesticides and micronutrients may be adsorbed on the clay substrate, undergo an exchange with cations or anions of the clays, cause a variation of the nutrient availability and microorganism of the soil and bring about various physicochemical changes in the clays and soils. The extent and mechanism of adsorption and exchange may affect the persistence, degradation, leaching and translocation of pesticides in soil environment.

In view of the great importance of such effects in modern agricultural production and environmental pollution it was considered important to examine the mechanism of interaction and adsorption of certain organic pesticides and their residues such as zinc, which is a micronutrient also, with a few selected clays, hitherto not investigated. The influence of an organic pesticide on the major nutrient availability of two selected Indian soils was also studied. The principles of electrometric behaviour at the reversible electrodes, adsorption isotherms, kinetics of exchange and thermodynamics of exchange equilibria, were freely used in the investigations.

The subject matter of the thesis entitled "Studies on Soil Colloid Pesticide Interactions" has been investigated on the following lines:

(i) Studies on the mechanism of adsorption of pesticides in clays: Parts I and II

(ii) Studies on the thermodynamics of exchange in clays: Parts I and II

(iii) Studies on the kinetics of zinc exchange with Na-dickite

(iv) Studies on the influence of a pesticide (D-D mixture) on some nutrients of soils.

For investigations under (i) and (ii) above one organic and one inorganic ion was selected for interaction with clays. In view of a certain lack of information on the above aspects of clay and soil interactions it was considered that such studies will prove beneficial in several ways.

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C H A P T E R - I

STUDIES ON THE MECHANISM OF ADSORPTION OF PESTICIDES WITH CLAYS

PART I: Adsorption of nicotine with hydrogen and sodium saturated dickites.

PART II: Adsorption and reactions of zinc with hydrogen and sodium saturated dickites.

CHAPTER - I, PART - I

ADSORPTION OF NICOTINE WITH HYDROGEN AND SODIUM SATURATED DICKITES

I N T R O D U C T I O N

A study of the adsorption of simple organic molecules plays an important part in understanding the mechanism of their interactions with soil clays. Adsorption of organic compounds on clay surfaces depends upon several factors[1,2] such as strong cation dipole attractions[3], hydrogen bonding[4], solvation of cations by polar molecules, coordination[5], cation exchange reactions, van der Waals interactions[4], pH and other environmental conditions.

Clay minerals constitute the most important reactive surfaces of the soil. They have been reported to provide heterogeneous chemical spots in the form of sorbed water around cations[6], hydroxyls at the edges, lattice surface oxygens and electrical double layer of changing polarity[7] at the edges. They possess electron accepting sites in the form of exposed aluminium[8] and transition metals in higher valency state at the edges. The location[9] and distribution of exchange sites on clays is an important factor in the nature and extent of adsorption.

The mineral dickite, a polymorph of $Al_4(Si_4O_{10})(OH)_8$, has a structure somewhat similar to kaolinite. It is believed to carry Lewis and Bronsted acidic sites on its edge crystal

✣ Dickite is one of the important clay minerals of the kaolinite group and is found to exist in a high degree of purity and crystallinity. Relatively less work has been reported on this clay mineral; therefore, it is thought proper to utilise this clay for the study of adsorption of organic molecules, like nicotine, and inorganic ions, such as Zn^{2+}, and also for kinetic studies, which suggest the reaction mechanism of solute at clay interface.

faces[10]. Fordham[11] has demonstrated the existence of positive and negative sites at the edges of dickites along with some basal surfaces. The behaviour of such clay minerals, both chemically and physically depends to a great extent upon their surface energetics.

Nicotine is a polar heterocyclic compound. It is an electron donor in which the aliphatic nitrogen of the pyrrolidine ring is the donor species. It is an important pesticide. Its importance in the functions of the central nervous system is well known. A study of the adsorption and interaction of pesticides is of great importance because processes such as effective pesticidal action, their mobility, persistence and toxicity[12] in soils depend to a great extent upon the nature and interaction of the chemical with the silicate clays[13].

Adsorption isotherms and titration curves can be used to provide information on the mechanism of interaction of organics with soils. Regular and discontinuous isotherms[14] due to heterogeneities on the adsorbant surface have been observed. Giles et al.[15] have classified the various shapes of adsorption isotherms with respect to the reaction mechanism concerned.

✣

The primary objective of this work was to investigate the mechanism of adsorption and interaction of nicotine, a typical alkaloid on dickite, a void filling mineral of the algal limestones in its acid and base saturated forms in dilute clay water suspensions.

Organic matter from dickite clay was removed by treating the clay with excess of hydrogen peroxide and further the excess of hydrogen peroxide was completely decomposed by heating till no effervescence is released by peroxide.

△ Freshly prepared H-dickite[1] was used in all these experiments to avoid Al-migration from lattice layers though other cation saturated clays are quite stable.

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EXPERIMENTAL

The clay mineral used in these studies was dickite. It was an American sample collected from Mexico and verified as a monomineralic standard under the direction of Dr.Ralph J. Holmes of the Columbia State University. It was supplied by Ward's Natural Science Establishment Inc., Rochester, New York. Less than 2 μ clay fraction was separated from this mineral by oxidising its organic matter and dispersing it by grinding lightly with a pestle and mortar with distilled water followed by centrifugation at a speed of 3500 rpm in the "International Chemical" centrifuge.

PREPARATION OF SODIUM AND HYDROGEN SATURATED DICKITES

Aldrich and Buchanan's[16] method was used for the preparation of homoionic clay samples. The less than 2 μ suspension obtained above was converted into sodium dickite by saturating it several times with molar sodium chloride solution and 0.1N HCl. The sodium clay was then washed with distilled water till the clay dispersed and the supernatant showed a negative test for chloride and till its conductivity became constant (order, 10^{-5} mhos per cm).

A part of the above sodium saturated clay suspension was converted in hydrogen saturated dickite by passing it through a column of H-Dowex-50W-X8 cation exchange resin at a speed of 3 ml per minute several times till the pH and conductance of the suspension became constant. It was then quickly used for adsorption experiments to avoid decomposition.

DETERMINATION OF THE CONCENTRATION OF SUSPENSIONS

The concentration of the suspensions were determined by evaporating a known volume of each suspension in a petri dish. The concentration of the suspensions varied from 2.0 to 9.0 g per litre.

POTENTIOMETRIC AND CONDUCTOMETRIC TITRATIONS

Freshly prepared samples of acid and base saturated dickites were then subjected to potentiometric and conductometric titrations with nicotine and sodium hydroxide. To 10 ml each of the acid and base saturated suspensions taken in a number of pyrex glass tubes; varying concentrations of the nicotine solution (0.5 g per litre) were added and the volume made constant with distilled water. The tubes were shaken for 3 hours each day for three days at 30 $\pm$ 1°C. The same procedure was also carried out with a standard solution of NaOH (0.103N and 0.003N).

The pH changes were then recorded with Elico pH meter, model Li-10 with saturated calomel and glass electrode assembly. Conductivity variations were also noted with the help of Philips conductivity meter with dip type cell. The results obtained for pH and conductivity changes are recorded in tables (I to IV) and represented vide Figs.2 and 3.

ADSORPTION OF NICOTINE BY DICKITE

The adsorption experiments were done by taking 10 ml of clay suspensions in a large number of glass stoppered tubes and

adding varying concentrations of the nicotine solution (0.5 g per litre) and adjusting the mixture to a constant volume with distilled water. The tubes were shaken for three hours each day for three days at 30 ± 1°C to attain equilibrium. The mixtures were then allowed to stand overnight, the supernatant liquids taken out, centrifuged and the residual nicotine estimated with standard hydrochloric acid solution using methyl red as indicator. The difference between the amount of nicotine added and remaining after contact with clay gave the amount of nicotine adsorbed by the clay. The results of adsorption are given in tables V and VI and represented vide Fig.4.

X-RAY ANALYSIS

X-ray analysis was carried out on acid and base saturated samples of dickite and on nicotine treated dickite complexes. For this purpose a small quantity of the hydrogen as well as sodium saturated dickite suspension was placed on glass slides and allowed to dry at room temperature be give well oriented layers of the homoionic clay samples.

For x-ray study of the nicotine dickite complexes, hydrogen and sodium saturated dickite clay suspensions were treated with nicotine solution upto a concentration of maximum adsorption in each of the cases. They were then dried over glass slides to form a well oriented layer.

Some of the nicotine treated samples were also solvated with glycerine and same subjected to heat treatment in a muffle

furnace at 550°C for 2 hours before x-ray analysis.

All the oriented samples mentioned above were then subjected to x-ray examination using filtered CuK$_\alpha$ radiation on a "Mikrometa" goniometer at a scanning speed of 2 degrees 2θ per minute. Basal spacings in Å deduced from the position of 001 reflections and ASTM cards of the x-ray data file are recorded in table VII.

INFRARED ANALYSIS

An attempt was made to utilise the infrared technique for characterising the type of complex formed between the homoionic dickites and nicotine.

For this purpose, 25 ml of the hydrogen and sodium saturated dickite suspensions and the suspension of their nicotine complexes at the point of maximum adsorption were taken. Thin self supporting films of the clay suspensions were made by slow evoporation of the suspensions on polythene plates. The films obtained were, however, too brittle and did not possess sufficient strength to hold them in the sample holder for infrared analysis. Since treatment of the complexes with KBr and KNO_3 in amounts upto five times of the BEC and repeated washing with deionised water did not result in any release of nicotine, from the complexes it appeared that it was strongly adsorbed on the clay surface and KBr technique could be used for infrared analysis.

For this purpose about one miligram of the 200 mesh powder of the samples were mixed with about 100 mg of previously dried KBr powder (Merck's pure grade). The mixtures were then finely ground

in an agate mortar and pressed into transparent discs using a hydraulic press and steel die. The samples were then mounted in sample holders and the infrared spectra recorded on the Beckman IR-20 double beam grating spectrophotometer in the region 500-3800 cm^{-1}. The results are given in table VIII. The abbreviations used and the intensities estimated against the absorption bands are denoted by the following letters in the tables. B = broad, Sh = sharp, Vs = very strong, S = strong, M = medium, W = weak and Vw = very weak.

TABLE I

pH and conductivity variations during adsorption of nicotine on hydrogen saturated dickite

Concentration of clay suspension	= 2.42 g per litre
Volume of clay suspension	= 10.0 ml
Strength of nicotine solution	= 0.5 g per litre
Total volume of mixture (clay suspension + nicotine + water)	= 25.0 ml

Volume of nicotine solution added in ml	Amount of nicotine added in meq. per 100 g clay	pH of the equilibrium suspension	Conductance x 10^{-5} mhos cm^{-1}
0.0	0.0	4.95	35.6
0.5	6.4	6.80	33.7
1.0	12.7	6.85	33.3
1.5	19.1	7.55	29.2
2.0	25.4	7.75	32.9
3.0	38.1	7.85	37.6
5.0	63.5	8.05	37.7
7.5	95.3	8.35	47.0
10.0	127.0	8.50	47.0
12.5	158.8	8.75	47.0

TABLE II

pH and conductivity variations during adsorption of nicotine on sodium saturated dickite

Concentration of clay suspension = 8.76 g per litre

Volume of clay suspension taken = 10.0 ml

Strength of nicotine solution = 0.5 g per litre

Total volume of mixture (clay suspension + nicotine + water) = 25.0 ml

Volume of nicotine solution added in ml	Amount of nicotine added in meq. per 100 g clay	pH of the equilibrium suspension	Conductance x 10^{-5} mhos cm^{-1}
0.0	0.0	6.05	7.7
0.5	1.8	6.10	6.9
1.0	3.5	6.20	6.9
1.5	5.3	6.65	6.9
2.0	7.0	6.80	6.9
3.0	10.6	6.85	6.9
5.0	17.6	7.20	7.7
7.5	26.4	7.40	8.8
10.0	35.2	7.40	8.8
12.5	44.0	7.40	9.4

TABLE XII

pH and conductivity variations during the interaction between nicotine and hydrogen saturated dickite

Concentration of clay suspension = 2.85 for pH and 1.47 g for conductance per litre respectively

Volume of clay suspension taken = 10.0 ml

Strength of nicotine solution = 0.5 g per litre

Total volume of mixture (volume of clay suspension + nicotine + water) = 25.0 ml

Amount of nicotine added in meq. per 100 g clay	pH of the equilibrium suspension	Amount of nicotine added in meq. per 100 g clay	Conductance x 10^{-5} mhos cm^{-1}
0.0	4.05	0.0	43.8
1.1	4.10	2.1	28.6
2.2	4.10	4.2	26.8
3.2	4.35	6.3	26.3
4.3	4.45	8.4	25.3
5.4	4.40	10.5	25.4
8.1	4.70	12.6	25.4
10.8	4.75	14.7	28.6
21.6	6.20	16.8	28.5
32.4	8.00	18.9	28.6
43.2	8.15	21.0	28.6
54.0	8.55	23.1	28.6
64.8	8.65	27.2	28.6

TABLE IV

pH and conductivity variations during the interaction between NaOH and hydrogen saturated dickite

Concentration of clay suspensions = 12.57 g for pH and 2.22 g for conductance per litre respectively

Volume of clay suspension = 25.0 and 10.0 ml

Strength of NaOH solutions = 0.103N and 0.003N

Total volume of clay suspension taken (clay suspension + NaOH + water) = 30.0 ml

Amount of NaOH added in meq. per 100 g clay	pH of the equilibrium suspension	Amount of NaOH added in meq. per 100 g clay	Conductance x 10^{-5} mhos cm^{-1}
0.0	3.35	0.0	23.9
3.3	3.45	1.4	25.8
4.9	3.80	2.7	25.3
6.6	4.27	4.1	24.4
9.8	6.10	5.4	24.4
11.5	6.70	6.8	21.9
13.1	8.20	10.1	21.2
16.4	9.65	13.5	22.3
18.0	9.85	16.2	22.3
19.7	10.10	27.0	14.9
23.0	10.30	40.5	12.0
26.2	10.50	54.0	10.3
32.8	10.70	67.5	11.2

TABLE V

Adsorption of nicotine by hydrogen saturated dickite

Concentration of clay suspension	= 2.42 g per litre
Volume of clay suspension	= 10.0 ml
Strength of nicotine solution	= 0.5 g per litre
Strength of HCl solution	= Strength of nicotine solution
Indicator used	= Methyl red
Total volume of mixture (clay suspension + nicotine + water)	= 25.0 ml

Volume of nicotine solution added in ml	Volume of HCl required to titrate residual nicotine in ml	Equilibrium concentration of nicotine in supernatant liquid in mmoles per litre	Nicotine adsorbed in mmoles per 100 g clay
0.0	0.00	0.00	0.0
0.5	0.00	0.00	6.4
1.0	0.00	0.00	12.7
1.2	0.00	0.00	15.2
2.0	1.00	0.12	12.7
3.0	1.50	0.18	19.1
5.0	2.80	0.33	28.6
7.5	4.55	0.54	37.5
10.0	7.05	0.84	37.5
12.5	9.40	1.13	39.4

TABLE VI

Adsorption of nicotine by sodium saturated dickite

Concentration of clay suspension = 8.76 g per litre

Volume of clay suspension = 10.0 ml

Strength of nicotine solution = 0.5 g per litre

Strength of HCl solution = Strength of nicotine solution

Indicator used = Methyl red

Total volume of mixture (clay suspension + nicotine + water) = 25.0 ml

Volume of nicotine solution added in ml	Volume of HCl required to titrate residual nicotine in ml	Equilibrium concentration of nicotine in supernatant liquid in mmoles per litre	Nicotine adsorbed in mmoles per 100 g clay
0.0	0.00	0.00	0.00
0.5	0.25	0.03	0.88
1.0	0.50	0.06	1.76
1.5	1.25	0.15	0.88
2.0	1.50	0.18	1.76
3.0	2.75	0.33	0.88
5.0	4.50	0.54	1.76
7.5	6.75	0.81	2.63
10.0	7.25	0.87	9.63
12.5	8.50	1.02	14.00

TABLE VII

Basal spacings of hydrogen, sodium, nicotine, glycerine and heat treated samples of dickite

Nature of dickite	Basal spacings at 001 reflections in angstroms	Interlamellar separation in angstroms
H-saturated dickite	7.07 (S)	-
Nicotine treated H-dickite	7.13 (W)	0.06
Na-saturated dickite	7.05 (S)	-
Nicotine treated Na-dickite	7.00 (M)	Nil
Nicotine complex treated with glycerine	7.00 (W)	Nil
Na-saturated dickite at 550°C	Collapsed	-
Nicotine complex at 550°C	Collapsed	-

Letters in parenthesis in column II indicate intensities:

S = Strong, M = Medium and W = Weak.

TABLE VIII

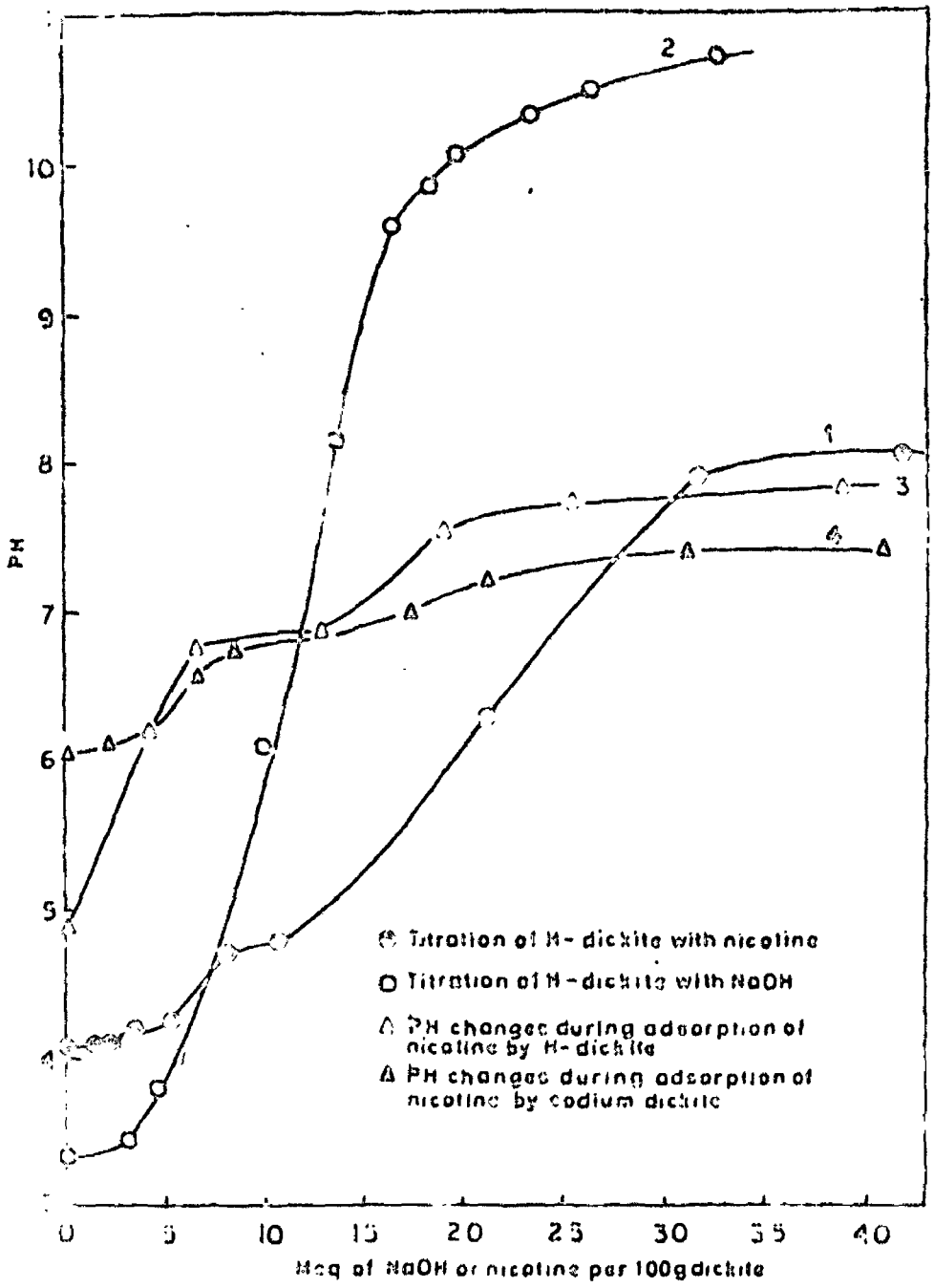
Infrared band assignments of nicotine, H-dickite and H-dickite nicotine complex

Nicotine cm^{-1}	H-dickite cm^{-1}	H-dickite nicotine complex cm^{-1}	Assignment
-	3600 (Vw.)	3630 (Vw.)	OH stretching
3030 (Vw.)	-	-	C-H stretching
2950 (B.M.)	-	-	C-H stretching
2780 (B.M.)	-	-	$N-CH_3$ bending
1550-1595 (Sh.S.)	-	-	C=C bending
1420-1450 (Sh.W.)	-	1400 (Sh.W.)	$N-CH_3$ ring stretching
715-805	1115 (Sh.W.)	1120 (Sh.W.)	Si-O-Si stretching band
-	1030 (Sh.M.)	1030 (Sh.M.)	Si-O-Si stretching band
-	990 (Sh.M.)	990 (Sh.M.)	Al-OH-Al bending
-	920 (Shoul-dering)	925 (Shoul-dering)	Al-OH-Al bending
-	790 (Sh.W.)	795 (Sh.W.)	Si-O-Al bending
-	740 (Sh.Vw.)	750 (Sh.Vw.)	Si-O-Al bending
-	675 (Sh.M.)	690 (Sh.W.)	Si-O-Al bending

RESULTS AND DISCUSSION

The results of potentiometric and conductometric titrations of H-dickite with NaOH and nicotine are given vide table IX, Figs.2 and 3. The figures (curves 3 and 4) also show the changes that occurred in the pH and conductance during adsorption of nicotine by acid and base saturated dickites. The figures in parentheses in the table indicate the pH at the inflection points. The meq. of base per 100 g clay as obtained from the inflections gave the base exchange capacities.

Adsorption of nicotine on acid and base saturated dickites in dilute suspensions in the equilibrium concentration range of 0.0 to 1.0 mmole of nicotine per litre yielded isotherms vide Fig.4. An examination of the isotherms revealed that the isotherm for hydrogen saturated dickite was similar to class 'H' isotherm as defined by Giles et al.[15] and that for the sodium saturated system similar to class 'L'. The adsorption in the two cases was thus very much different. The initial part in the case of the isotherm for the acid H-dickite was vertical indicating that nicotine had such a high affinity for the acid dickite that in dilute suspensions it was completely adsorbed till a limiting value (15.80 mmoles) was reached at a point corresponding to complete saturation of its base exchange capacity and a pH = 7.10. An inflection or "knee" occurred at this point indicating completion of the first degree saturation. Such an initial steep rise was indicative of chemisorption with edge to edge ion attraction[17]. An increase in pH (Fig.2, curve 3) and a decrease in electrical conductance (Fig.3, curve 3) with



POTENTIOMETRIC TITRATION OF DICKITE WITH NICOTINE AND NaOH AND CHANGE ADSORPTION

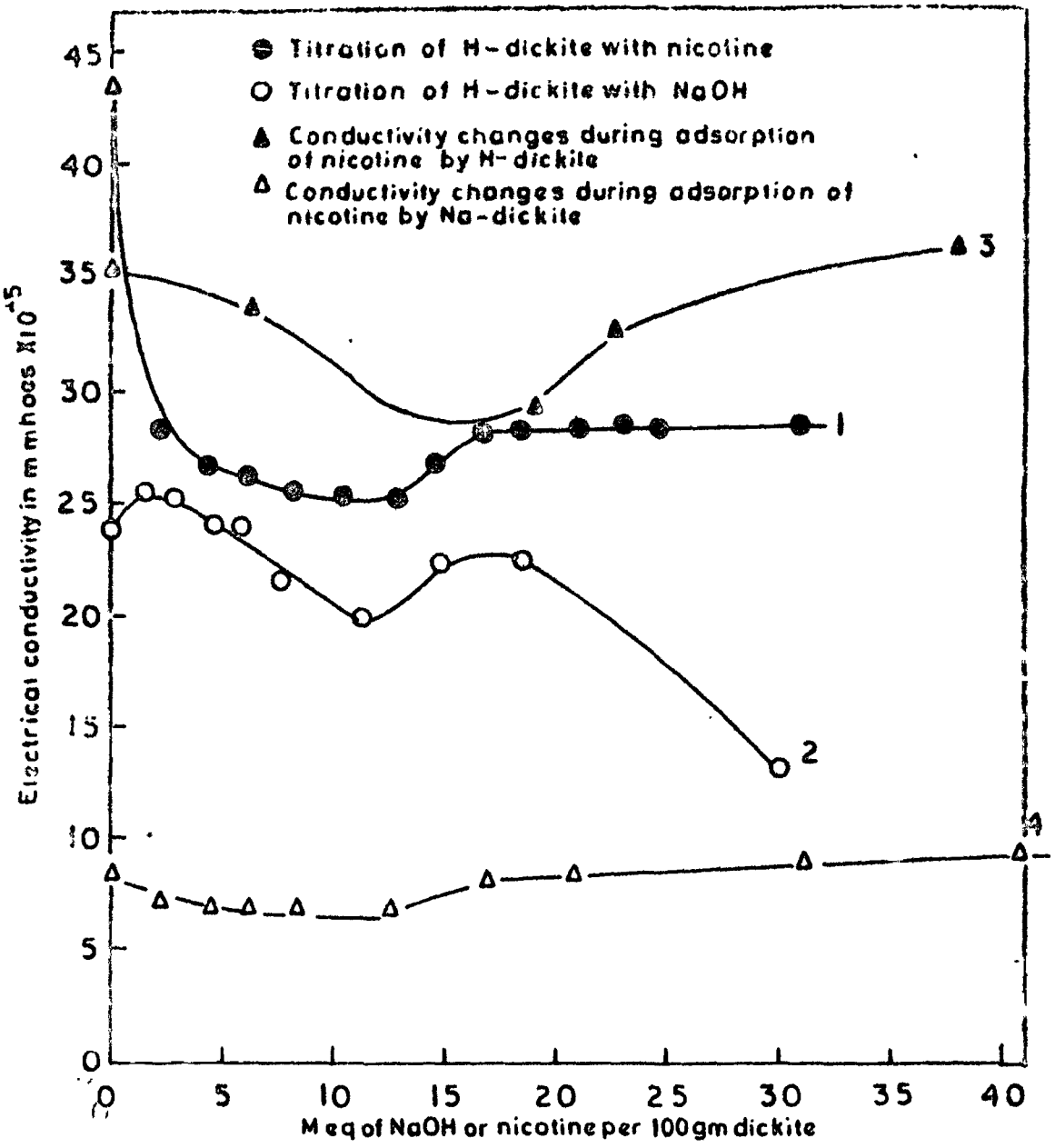


FIG. 3 CONDUCTOMETRIC TITRATION OF DICKITE WITH NICOTINE AND NaOH

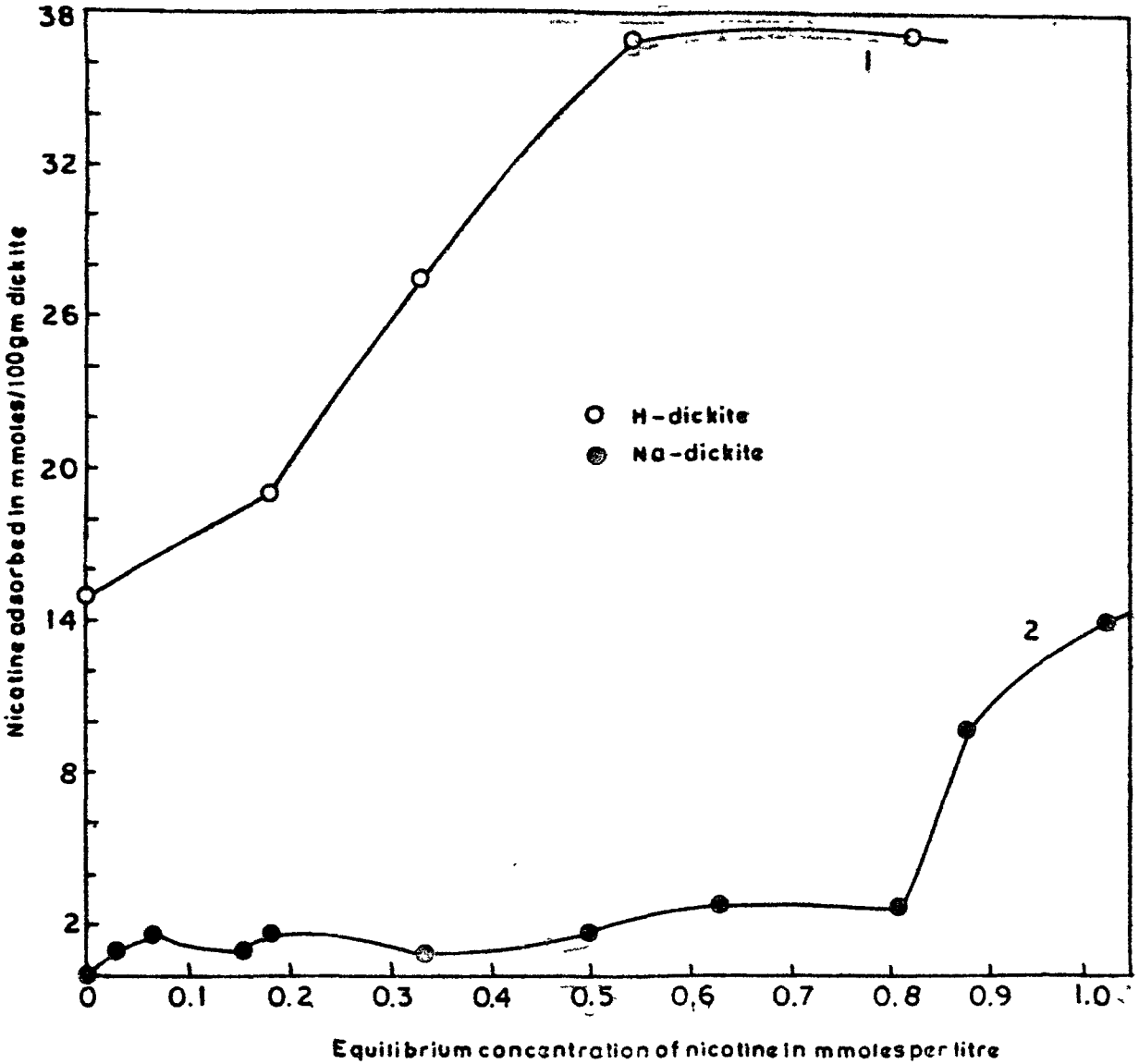


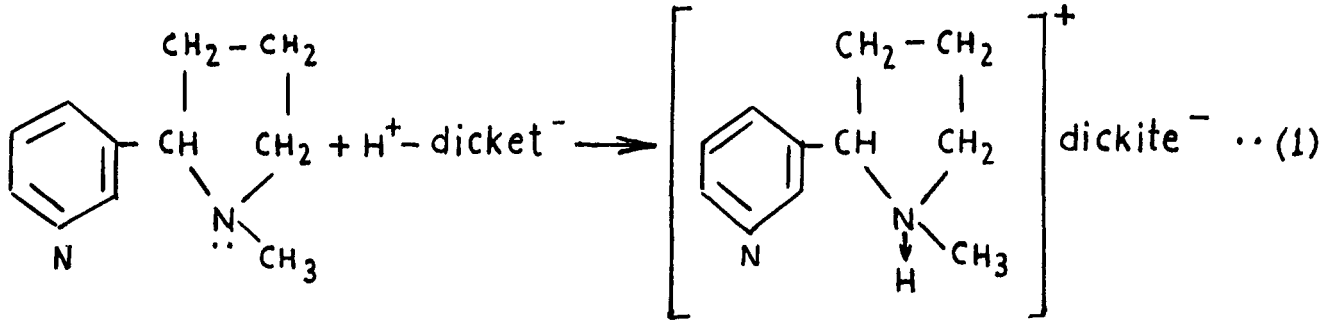
FIG. 4 ADSORPTION ISOTHERMS OF ACID AND BASE SATURATED DICKITES

TABLE IX

Main inflections and base exchange capacities of acid and base saturated dickites as obtained during titration and adsorption

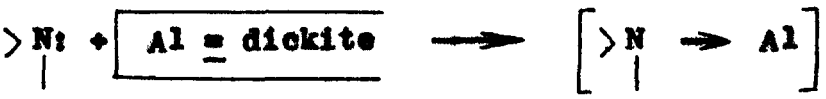
Mineral form	Nicotine as titrant and absorbate				Sodium hydroxide as titrant	
	Point titration		Changes during adsorption			
	Potentiometry	Conductometry	Potentiometry	Conductometry	Potentiometry	Conductometry
H-dickite	15.0(5.2)	12.5	15.0(7.1)	15.0	14.0(8.5)	12.5
Na-dickite	-	-	15.0(6.9)	12.5	-	-

an inflection similar to that obtained during titrations pointed to removal of protons during the interaction. The initial adsorption of nicotine on H-dickite, therefore, appeared to be due to the donation of electrons by nicotine to H-dickite resulting in coordination of its molecule as follows:



.. (1)

The subsequent rise in adsorption beyond the inflection (Fig.4, curve 1) pointed to an interaction of nicotine with the Bronsted[18] or Lewis acid[8] sites at the crystal edges of dickite. It has, however, been reported that Bronsted acid sites at the crystal edges of clays are not strong[19] enough to react with weak bases like pyridine. Hence in the case of nicotine the Lewis acid character of dickite edges appeared to predominate. With aluminium at the edges thus acting as an electrone acceptor and nicotine as an electron donor, a subsequent interaction resulted as follows:



.. (2)

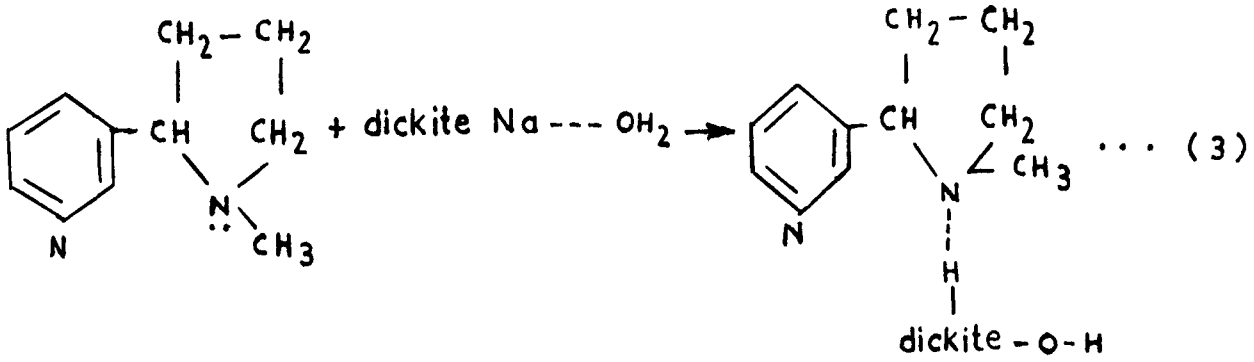
With the saturation of these sites the adsorption of nicotine in acid dickite became constant (Fig.4, curve 1). This found support from the pH and conductance changes which also became nearly constant (Figs.2-3, curve 3) at this stage.

Inspite of the greater deflocculation effect and larger surface area exposed by Na-dickite in comparison to H-dickite, a very small amount of nicotine was initially adsorbed by the sodium saturated dickite. This happened till an equilibrium concentration of 0.8 mmoles of nicotine was reached. As is often observed in cases of 'L' curves it thus appeared that nicotine molecules had some difficulty in finding vacant sites on the surface of Na-dickite. Fluctuations in the small adsorption were also observed in the earlier stages of the interaction suggesting changes from hydrophobic to hydrophilic nature in the clay system.

The nature of exchangeable cation in dickite thus seemed to determine the extent of adsorption. The order of adsorption found confirmation from the partial molar free energy changes that occurred during the interaction. The changes in partial molar free energy $\bar{F}$ were calculated from the thermodynamic relationship $-\bar{F} = RT \ln \frac{C_e}{C_o}$ where C_e and C_o were the equilibrium and initial concentration of the suspension respectively. An average of five values of $\bar{F}$ in case of H- and Na-saturated dickites yielded 301.0 and 204.3 cal/mol respectively, thus confirming the extent of the driving force available for the adsorption of nicotine on the dickites.

The small amount of nicotine adsorbed in the earlier concentration range by Na-dickite and its marked difference from that observed in acid clay suggested that nicotine was adsorbed in this range through comparatively weak adsorptive forces at a binding site different from that in the case of the acid system.

The interaction of nicotine with Na-dickite can be ascribed to formation of coordination bonds, capacity of nicotine to desorb water from around Na^+ ions giving rise to proton transfers, hydrogen bonding with directly coordinated water and interaction with the weakly acidic sites at the edges. Possibility of coordination of nicotine to Na^+ ions or proton transfers from adsorbed water would result in significant conductivity changes which were not observed in the present case. The small amount of adsorption of nicotine on Na-dickite in the early stages, therefore, appeared to be due to formation of hydrogen bonds between the pyrrolidine nitrogen of nicotine and the coordinated water as follows:



... (3)

With the saturation of the above sites and crossing of the energy barrier, the electron acceptor Al or the weakly acidic hydroxyls at the edges of dickite took over and a sudden jump in chemisorption occurred vide equation (2), as in the case of acidic dickite, (Fig.4, curve 2), or vide equation (4) as follows:

... (4)

There is evidence that clay surfaces even when saturated with basic cations act as weak to moderately weak acids[6].

Examination of the nicotine-dickite complexes under x-ray diffraction did not yield any marked increase in basal spacing (table VII). Treatment of the complex with glycerine showed no variation. Heat treatment at 550°C resulted in a complete collapse of the dickite peaks. These observations were in line with the fact that no lateral surface was available in dickite for the interaction with nicotine and only the edge sites took part in the interaction.

Some of the propositions made above found support from infrared studies. The N-CH_3 stretching band in nicotine in the range 1420-1450 cm^{-1} showed a shift in frequency to 1400 cm^{-1}. This shift appeared to be in accordance with protonation of nicotine by H-dickite at the pyrrolidine ring nitrogen as represented by equations 2, 3 and 4 given above. Further a spectral shift of H-dickite from 675cm^{-1} to 690 cm^{-1} supported an interaction of nicotine at the crystal edges of dickite as indicated in equation 2. Further work in infrared spectroscopy with self supported dickite films and its complexes with nicotine in higher concentration ranges is, however, necessary to fully confirm infrared inferences on the above reaction mechanisms.

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CHAPTER - I, PART - II

ADSORPTION AND REACTIONS OF ZINC WITH HYDROGEN AND SODIUM SATURATED DICKITES

I N T R O D U C T I O N

Among the micronutrients zinc salts have been recognised as valuable fertilisers and spray materials. Zinc formulations such as the dithiocarbamates of zinc like zineb and ziram are widely used as fungicides and insecticides. Their degradation leaves zinc residues. Some plants like tomato and paddy are able to adsorb zinc from these compounds with beneficial and toxic effects. Other compounds such as zinc sulphate are used as fertilizers to cure zinc deficiency. Consequently the adsorption of zinc and its reactions with clays and soils have received increased attention during the last few decades.

Elgabaly and Jenny[1] showed that part of the zinc sorbed by montmorillonite could not be exchanged by ammonium acetate and it reduced the exchange capacity. Tiller and Hodgson[2] showed that silicate clays adsorbed zinc by cation exchange and irreversibly by lattice penetration. Bingham, Page and Sims[3] found that zinc could be an exchangeable cation and amounts in excess of CEC were retained as hydroxide which became unavailable due to fixation. Thus the activity of zinc in clays is due to several simultaneous interactions which are worth investigating.

The amount of zinc interacting with clays of different cation forms depends upon time of reaction, pH of the system, and

EXPERIMENTAL

The clay mineral used in these investigations was dickite collected from Ward's Natural Science Establishment, Inc., Rochester, New York. It was verified as a monomineralic standard under the direction of Dr.Ralph J. Holmes of the Columbia State University. The mineral was broken up in a mortar using a rubber covered pestle. The organic matter was oxidised with hydrogen peroxide and the mixture diluted with distilled water. The clay was then dispersed by electrical stirring. Less than 2 micron dickite fraction was obtained by centrifugation at a speed of 3500 rpm in "International Chemical" centrifuge.

PREPARATION OF SODIUM AND HYDROGEN SATURATED DICKITES

Sodium and hydrogen saturated dickites[9] were prepared from the above dickite suspensions by the methods as described earlier in Part I of this Chapter.

DETERMINATION OF CONCENTRATION OF DICKITE SUSPENSIONS

The concentrations of the sodium and hydrogen dickite suspensions were determined by evaporating 10 ml each of the clay suspension in petri dishes of known weight and drying the residues at 105°C in an oven and finally determining the constant weight of the residues. The concentrations of sodium and hydrogen dickite suspensions were 20.0 and 16.4 g per litre respectively.

CATION EXCHANGE CAPACITY

The base exchange capacity of the dickite was determined

by Ganguli's[10] method. 25 ml of the hydrogen saturated dickite suspension was taken in a 250 ml glass stoppered pyrex conical flask. One gram solid KCl was added to this suspension, the flask was then shaken for half an hour and left overnight. The exchanged acidity was titrated with 0.1N KOH solution using phenolphthalein as indicator. From the amount of KOH solution required to neutralise the acidity, the BEC of the dickite was calculated. Its value was found to be 15 meq. per 100 g clay.

DETERMINATION OF ZINC

In the adsorption experiments zinc was estimated in the supernatant liquids by versenate titration using eriochrome black T as indicator at a pH value of 10.0.

For this purpose 5 ml portions of supernatant liquids were taken in a beaker, treated with 5 ml of a buffer of pH = 10, and three drops of eriochrome black "T" indicator. The contents were then titrated with standard E.D.T.A. solution to a blue end point. From the value of E.D.T.A. solution used up (minus the blank reading), the amount of zinc in solution phase was calculated.

EFFECT OF TIME ON ADSORPTION OF ZINC BY HYDROGEN AND SODIUM SATURATED DICKITES

For a study of the effect of time on zinc adsorption by dickite, five sets of 10 ml suspensions of H and Na-dickites were treated at 25°C with 0.5, 1, 2 and 7 ml of 0.04N $Zn(NO_3)_2$ solution. Further one set with 7 ml of $Zn(NO_3)_2$ and 10 ml of Na-dickite was also treated at 50°C. The mixtures were shaken for 15 minutes.

Similar experiments were carried out at 30, 45, 60 and 180 minutes. The mixtures were then centrifuged and zinc estimated in the supernatants by EDTA titration. The extent of adsorption was estimated as the difference between the amount of zinc added and remaining in the supernatants. The results are presented in tables X and XI and Figs.5 and 6.

EFFECT OF pH ON ADSORPTION OF ZINC BY SODIUM SATURATED DICKITE

For a determination of the effect of pH on zinc adsorption, sodium saturated dickite suspensions were treated with standard solutions of HNO_3 (0.1N) and NaOH (0.1N) respectively, to obtain the desired equilibrium levels of pH (3.0, 5.0, 6.0 and 7.0). The adsorption of zinc was then carried out at 25°C at each of the above pH values and at time intervals of 3 hours as described earlier. The results are given in table XII, Fig.7.

ADSORPTION OF ZINC BY DICKITE

The adsorption experiments were conducted by taking 10 ml each of the H- and Na-dickite suspensions in a large number of glass stoppered tubes and adding varying amounts of 0.04N $Zn(NO_3)_2$ solution. The mixtures were diluted to 25 ml with distilled water and shaking the tubes at 25°C in the first set of experiments and at 50°C in the second set for 3 hours in each case. The suspensions were then centrifuged and the residual zinc estimated with standard E.D.T.A. solution as described earlier. The difference gave the amount of zinc adsorbed. The results of adsorption are given in tables XIII to XVI, Fig.8.

TABLE X

Adsorption of zinc by hydrogen saturated dickite as affected by time

Concentration of clay suspension = 16.4 g per litre

Volume of clay suspension taken = 10.0 ml

Strength of zinc nitrate solution = 0.04N

Total volume of mixture = 25.0 ml

Temperature of experiment = 25°C

Volume of zinc nitrate added in ml	Meq. of zinc added 'a'	Time in minutes	Volume of 0.04N EDTA solution used in titration in ml	Zinc adsorbed in meq. per 100g clay 'x'	Rate constant $k_1 = \frac{2.303}{t}\log\frac{a}{a-x} \times 10^{-3}$	Half time of reaction $t_{\frac{1}{2}} = 0.693/k_1$ min^{-1}
0.5	12.2	15	0.47	0.7	3.94	175.9
		30	0.45	1.2	3.44	201.5
		45	0.43	1.8	3.55	195.2
		60	0.40	2.5	3.72	186.3
		180	0.40	2.5	1.24	558.9
1.0	24.4	15	0.91	2.2	6.58	105.3
		30	0.83	4.2	6.29	110.2
		45	0.75	6.1	6.27	110.5
		60	0.70	7.3	6.02	115.1
		180	0.70	7.3	2.00	346.5
2.0	48.8	15	1.86	3.4	4.81	144.1
		30	1.74	6.4	4.60	150.7
		45	1.68	9.2	4.64	149.4
		60	1.53	11.5	4.43	156.4
		180	1.53	11.5	1.60	433.1
7.0	170.8	15	6.70	7.3	2.92	273.3
		30	6.50	12.2	2.47	280.
		45	6.22	19.0	2.62	264.5
		60	6.10	22.0	2.23	302.6
		180	6.00	24.3	0.86	805.8

TABLE XI

Adsorption of zinc by sodium saturated dickite as affected by time

Concentration of clay suspension = 20.0 g per litre

Volume of clay suspension taken = 10.0 ml

Strength of zinc nitrate solution = 0.04N

Total volume of the mixture = 25.0 ml

Temperatures of experiment = 25°C unless otherwise stated

Volume of zinc nitrate added in ml	Meq. of zinc added 'a'	Time in minutes	Volume of 0.04N EDTA solution used in titration in ml	Zinc adsorbed in meq. per 100g clay 'x'	Rate constant $k_1 = \frac{2.303}{t}\log\frac{a}{a-x} \times 10^{-3}$	Half time of reaction $t_{\frac{1}{2}} = 0.693/k_1$ min^{-1}
0.5	10	15	0.46	0.8	5.57	124.4
		30	0.43	1.4	5.03	137.8
		45	0.39	2.2	5.01	138.3
		60	0.37	2.6	5.01	138.3
		180	0.37	2.6	1.67	415.0
1.0	20	15	0.91	1.8	6.65	104.2
		30	0.83	3.4	6.19	111.9
		45	0.75	5.0	6.40	108.3
		60	0.68	6.4	6.43	107.8
		180	0.68	6.4	2.14	323.8
2.0	40	15	1.83	3.4	6.13	113.1
		30	1.67	6.6	5.91	117.3
		45	1.56	8.8	5.55	124.0
		60	1.46	10.8	5.61	123.5
		180	1.46	10.8	1.87	370.6
7.0	140	15	6.70	6.0	2.93	236.5
		30	6.50	10.0	2.48	279.4
		45	6.20	16.0	2.69	257.6
		60	6.10	18.0	2.30	301.3
		180	6.00	20.0	0.86	805.8
7.0	140 (30°C)	15	6.75	5.0	2.41	287.6
		30	6.58	8.4	2.07	334.8
		45	6.40	12.0	2.00	346.5
		60	6.20	16.0	2.20	315.0
		180	6.05	19.0	0.81	855.6

TABLE XII

Adsorption of zinc by sodium saturated dickite at different pH values

Concentration of clay suspension = 20 g per litre

Volume of clay suspension taken = 10.0 ml

Strength of zinc nitrate solution = 0.04N

Total volume of mixture = 25.0 ml

Temperature of experiment = 25°C

pH	Volume of zinc nitrate solution added in ml	Meq. of zinc added	Volume of 0.04N EDTA solution used in titration in ml	Zinc adsorbed in meq. per 100 g clay
3	0.5	10	0.40	2
	1.0	20	0.85	3
	2.0	40	1.80	4
	7.0	140	6.50	10
5	0.5	10	0.40	2
	1.0	20	0.80	4
	2.0	40	1.65	7
	7.0	140	6.25	15
6	0.5	10	0.40	2
	1.0	20	0.80	4
	2.0	40	1.65	7
	7.0	140	6.20	16
7	0.5	10	0.40	2
	1.0	20	0.80	4
	2.0	40	1.65	7
	7.0	140	6.00	20
9	0.5	10	0.35	3
	1.0	20	0.65	7
	2.0	40	1.55	9
	7.0	140	5.70	26

TABLE XIII

Adsorption of zinc by hydrogen saturated dickite at 25°C

Concentration of clay suspension = 16.4 g per litre

Volume of clay suspension taken = 10.0 ml

Strength of zinc nitrate solution = 0.04N

Total volume of the mixture = 25.0 ml

Volume of zinc nitrate added in ml	Meq. of zinc added	Volume of 0.04N EDTA solution used in titration in ml	Equilibrium concentration of zinc in mmoles per litre	Zinc adsorbed in meq. per 100 g clay
0.0	0.0	0.00	0.00	0.0
0.1	2.5	0.00	0.00	2.5
0.4	9.8	0.25	0.20	3.7
0.7	17.1	0.25	0.20	11.0
1.0	24.4	0.50	0.40	12.2
1.3	31.7	0.75	0.60	13.4
1.6	39.1	1.00	0.80	14.6
2.2	53.7	1.60	1.28	14.6
2.5	61.0	1.88	1.50	17.7
2.8	68.3	2.00	1.60	19.5
3.0	73.2	2.20	1.76	19.5
3.6	87.8	2.75	2.20	20.7
4.0	97.6	3.15	2.52	20.7

TABLE XIV

Adsorption of zinc by hydrogen saturated dickite at 50°C

Concentration of clay suspension = 16.4 g per litre

Volume of clay suspension taken = 10.0 ml

Strength of zinc nitrate solution = 0.04N

Total volume of the mixture = 25.0 ml

Volume of zinc nitrate added in ml	Meq. of zinc added	Volume of 0.04N EDTA solution used in titration in ml	Equilibrium concentration of zinc in mmoles per litre	Zinc adsorbed in meq. per 100 g clay
0.0	0.0	0.00	0.00	0.0
0.1	2.5	0.03	0.02	1.8
0.4	9.8	0.25	0.20	3.7
0.7	17.1	0.50	0.40	4.9
1.0	24.4	0.75	0.60	6.1
1.3	31.7	1.00	0.80	7.3
1.6	39.1	1.25	1.00	8.5
1.9	46.4	1.50	1.20	9.8
2.2	53.7	1.75	1.40	11.0
2.5	61.0	2.00	1.60	12.2
2.8	68.3	2.25	1.80	13.4
3.0	73.2	2.45	1.96	13.4
3.6	87.8	3.00	2.40	14.6
4.0	97.6	3.25	2.60	18.3

TABLE XV

Adsorption of zinc by sodium saturated dickite at 25°C

Concentration of clay suspension = 20.0 g per litre

Volume of clay suspension taken = 10.0 ml

Strength of zinc nitrate solution = 0.04N

Total volume of the mixture = 25.0 ml

Volume of zinc nitrate added in ml	Meq. of zinc added	Volume of 0.04N EDTA solution used in titration in ml	Equilibrium concentration of zinc in m moles per litre	Zinc adsorbed in meq. per 100 g clay
0.0	0.0	0.00	0.00	0.0
0.1	2.0	0.00	0.00	2.0
0.4	8.0	0.25	0.20	3.0
0.7	14.0	0.50	0.40	6.0
1.0	20.0	0.60	0.48	8.0
1.3	26.0	0.80	0.64	10.0
1.6	32.0	1.10	0.88	10.0
1.9	38.0	1.40	1.12	10.0
2.2	44.0	1.60	1.28	12.0
2.5	50.0	1.90	1.52	12.0
2.8	56.0	2.00	1.60	16.0
3.0	60.0	2.20	1.76	16.0
3.6	72.0	2.80	2.24	16.0
4.0	80.0	3.20	2.56	16.0

TABLE XVI

Adsorption of zinc by sodium saturated dickite at 50°C

Concentration of clay suspension = 20.0 g per litre

Volume of clay suspension taken = 10.0 ml

Strength of zinc nitrate solution = 0.04N

Total volume of the mixture = 25.0 ml

Volume of zinc nitrate added in ml	Meq. of zinc added	Volume of 0.04N EDTA solution used in titration in ml	Equilibrium concentration of zinc in mmoles per litre	Zinc adsorbed in meq. per 100 g clay
0.0	0.0	0.00	0.00	0.0
0.1	2.0	0.00	0.00	2.0
0.4	8.0	0.25	0.20	3.0
0.7	14.0	0.50	0.40	4.0
1.0	20.0	0.75	0.60	5.0
1.3	26.0	1.00	0.80	6.0
1.6	32.0	1.20	0.96	8.0
1.9	38.0	1.40	1.12	10.0
2.2	44.0	1.70	1.36	10.0
2.5	50.0	2.00	1.60	10.0
2.8	56.0	2.20	1.76	12.0
3.0	60.0	2.25	1.80	15.0
3.6	72.0	2.85	2.28	15.0
4.0	80.0	3.25	2.80	15.0

RESULTS AND DISCUSSION

The amount of zinc adsorbed as a function of time is plotted in Fig.5 (a and b) for different concentrations of zinc nitrate added to the H- and Na-dickites respectively. Although the systems approached equilibrium from 1 to 3 hours, adsorption rapidly and then slowly increased with time. The initial rapid adsorption appeared to be due to reversible exchange between zinc ions and the replaceable H or Na ions of the dickite surface. The slower increase in adsorption after nearly 60 minutes was due to either a slow penetration of Zn^{2+} ions into the clay or fixation due to chemical forces. The reaction thus became more complex with lapse of time. Fig.5 (a and b) also showed that the amount of adsorption increased as more zinc ions were added to the aqueous suspension of clays.

Applying the simple kinetic rate laws, the order of reaction with respect to zinc was studied at different concentrations of zinc nitrate and at fixed concentration of the H- and Na-dickites. The initial reaction followed the first order kinetics (Fig.6, curves 1-9). Table XVII contain the representative results obtained in sets of experiments with different concentration of zinc nitrate added to H- and Na-dickites. The results showed that the values of rate constants were largely invariant in the initial stages of the first order reaction. Further the values of the rate constant increased with concentration of metal ion added upto a concentration of 24.4 meq. in H-dickite and 20 meq. in Na-dickite after which they decreased. On the other hand the half times of adsorption showed a

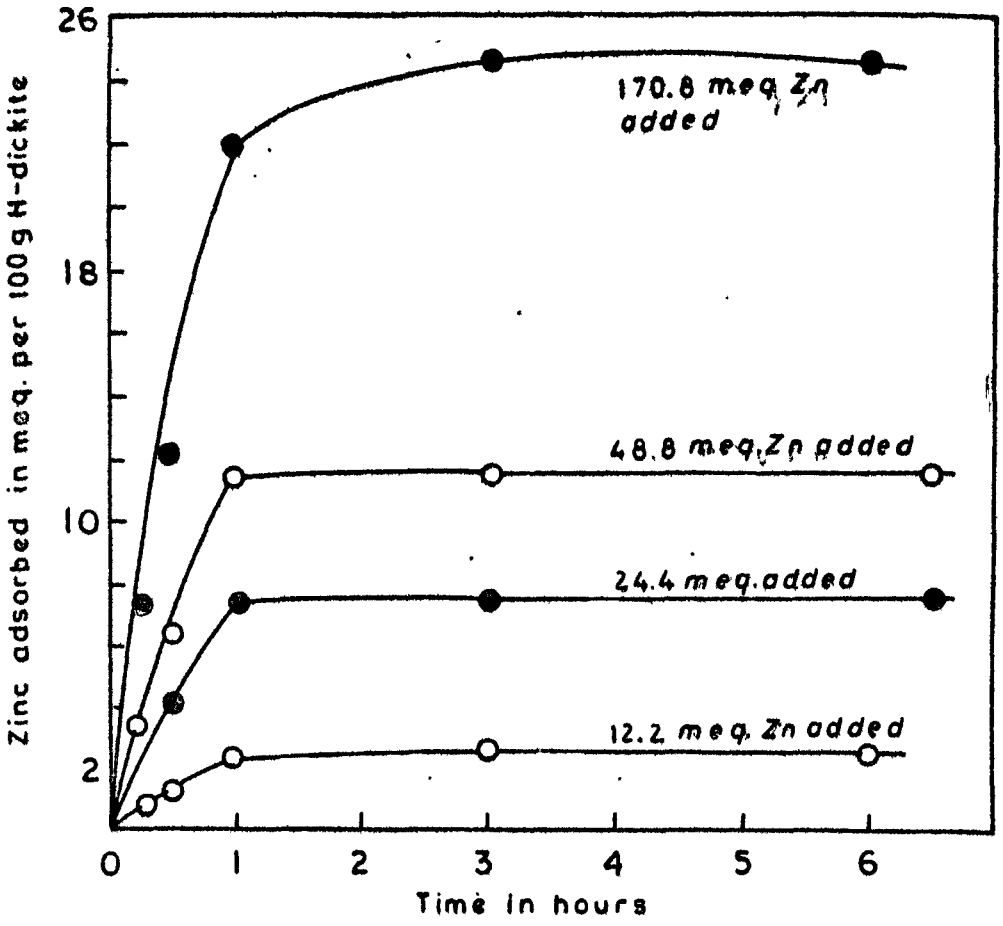

FIG. 5 a EFFECT OF TIME ON THE ADSORPTION OF ZINC BY H-DICKITE AT 25°C

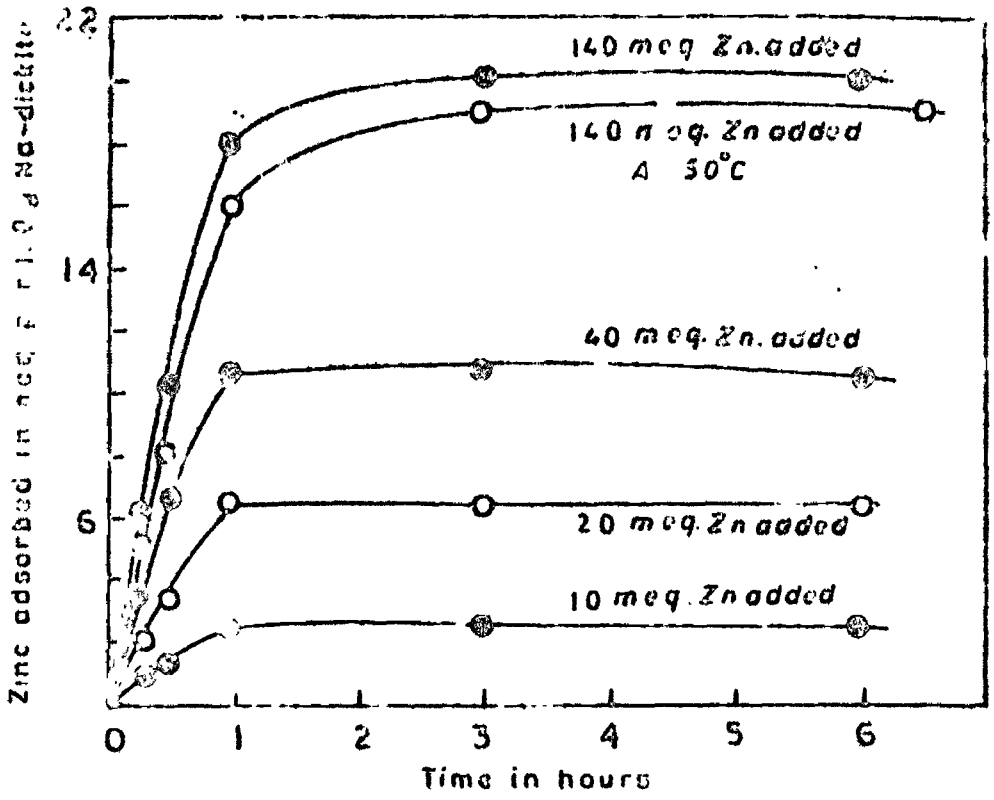

FIG. 5 b EFFECT OF TIME ON THE ADSORPTION OF ZINC BY Na-DICKITE AT 25° AND 50°C

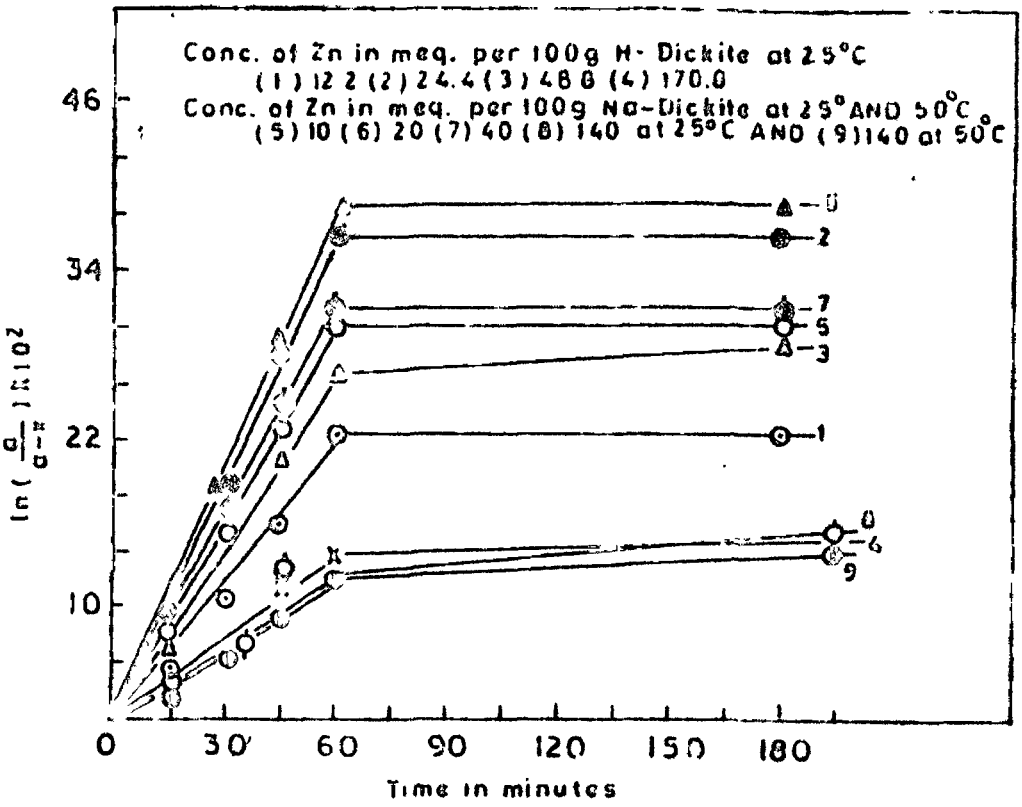

FIG 6 PLOTS OF $\ln\left(\frac{a}{a-x}\right)\times 10^2$ VS. TIME FOR THE REACTION BETWEEN ZINC NITRATE AND H- AND Na - DICKITE AT 25° AND 50°C

TABLE XVII

Effect of time on the reaction of zinc with H- and Na-dickite at pH 4.2 and 6.5 respectively

Time in minutes	H-dickite			Na-dickite		
	Conc. of zinc in meq/100 g clay	$K_1 \times 10^3 min^{-1}$	$t_{\frac{1}{2}}=0.693/k\ min^{-1}$	Conc. of zinc in meq/100 g clay	$K_1 \times 10^3 min^{-1}$	$t_{\frac{1}{2}}=0.693/k\ min^{-1}$
15		3.94	175.9		5.57	124.4
30		3.44	201.5		5.03	137.8
45	12.2	3.55	195.2	10.0	5.01	138.3
60		3.72	186.3		5.01	138.3
180		1.24	558.9		1.67	415.0
Average value		3.18	263.6		4.46	190.8
15		6.58	105.3		6.65	104.2
30		6.29	110.2		6.19	111.9
45	24.4	6.27	110.5	20.0	6.40	108.3
60		6.02	115.1		6.43	107.8
180		2.00	346.5		2.14	323.8
Average value		5.43	157.5		5.56	151.2
15		4.81	144.1		6.13	113.1
30		4.60	150.7		5.91	117.3
45	48.8	4.64	149.4	40.0	5.55	124.0
60		4.43	156.4		5.61	123.5
180		1.60	433.1		1.87	370.6
Average value		4.02	206.7		5.01	169.7

(Table XVII continued)

Time in minutes	H-dickite			Na-dickite		
	Conc. of zinc in meq/100 g clay	$k_1 \times 10^3 min^{-1}$	$t_{\frac{1}{2}}=0.693/k_1$ min^{-1}	Conc. of zinc in meq/100 g clay	$k_1 \times 10^3 min^{-1}$	$t_{\frac{1}{2}}=0.693/k_1$ min^{-1}
15		2.92	237.3		2.93	236.5
30		2.47	280.6		2.48	279.4
45	170.8	2.62	264.5	140.0	2.69	257.6
60		2.29	302.6		2.30	301.3
180		0.86	805.8		0.86	805.8
Average value		2.23	378.2		2.25	376.1
15		-	-		2.41	287.6
30		-	-		2.07	334.8
45	-	-	-	140.0	2.00	346.5
60		-	-		2.20	315.0
180		-	-	(at 50°C)	0.81	855.6
Average value		-	-		1.90	427.9

decrease and thereafter an increase with increase in the concentration of metal ion added. The initial behaviour upto a concentration of 24.4 meq. in H-dickite and 20 meq. in Na-dickite was characteristic of ion exchange processes controlled by film and possibly particle diffusion[4]. The reverse behaviour beyond the above concentration of zinc appeared to be due to a reaction mechanism other than exchange. It thus appeared that there was a difference in the mechanism of reaction of zinc with acid and base saturated dickites in the lower and higher ranges of zinc concentration.

Fig.7 illustrates the effect of pH on the adsorption of zinc by Na-dickite. At a low concentration, pH had almost no effect but as the concentration of zinc added to Na-clay increased, adsorption increased till either it became constant or continued to increase depending upon the concentration of zinc added. It appeared that a certain barrier had to be overcome before adsorption beyond the CEC occurred. Thus in the very high concentration range an almost continuous increase in adsorption with increase in pH appeared to be due to fixation and precipitation reactions as reported by earlier workers[11].

An examination of the adsorption isotherms in dilute suspensions in the equilibrium concentration range of 0 to 2.8 mmoles of zinc per litre (Fig.8) at 25° and 50°C indicated that the lower temperature isotherms (curves 1 and 3) for adsorption of zinc on H- and Na-dickite were similar to class "H" or high affinity plus class "C" or linear; and marked by plateaus as defined by Giles et al.[12] The initial part of the isotherm for

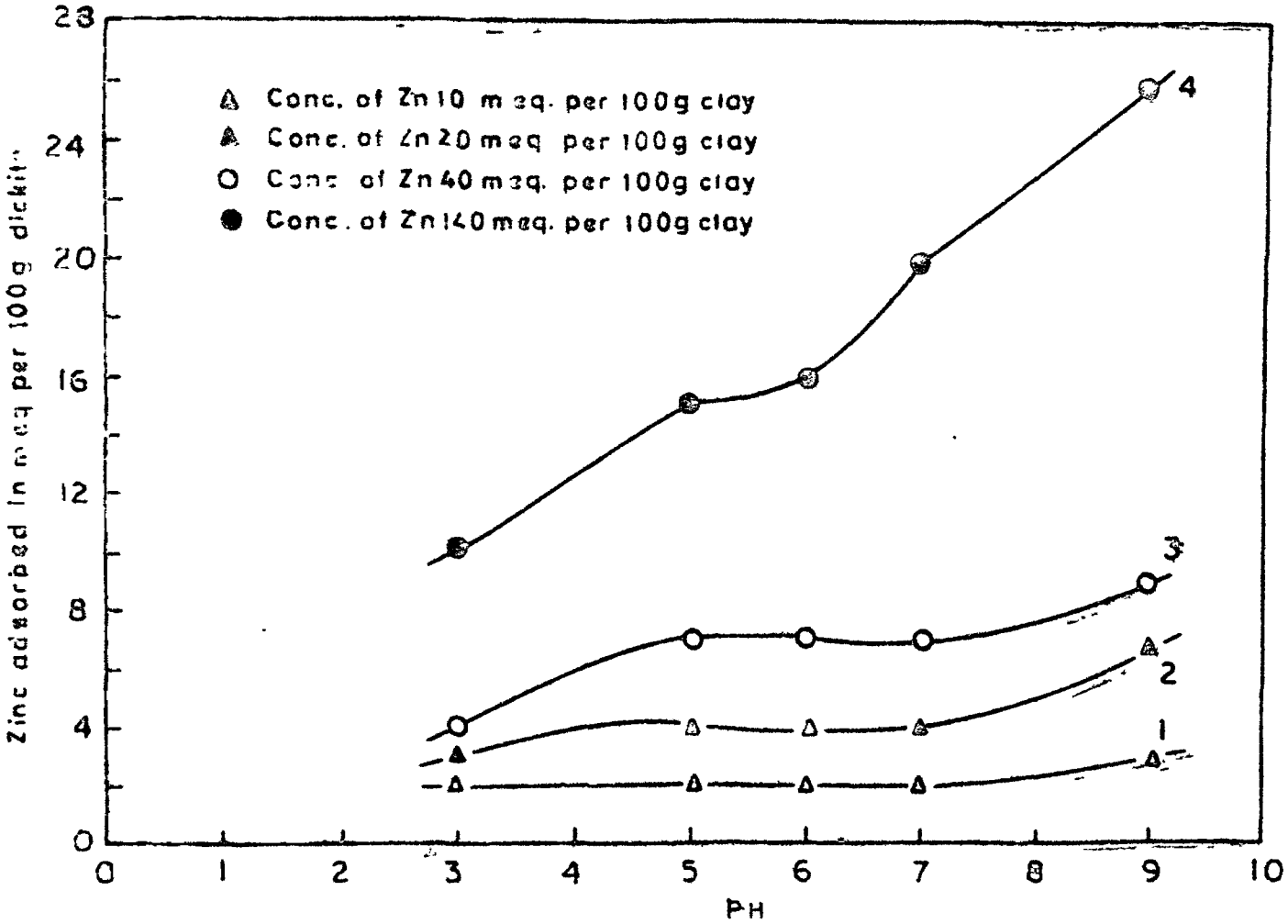

FIG. 7 EFFECT OF PH ON THE ADSORPTION OF ZINC ON SODIUM DICKITE

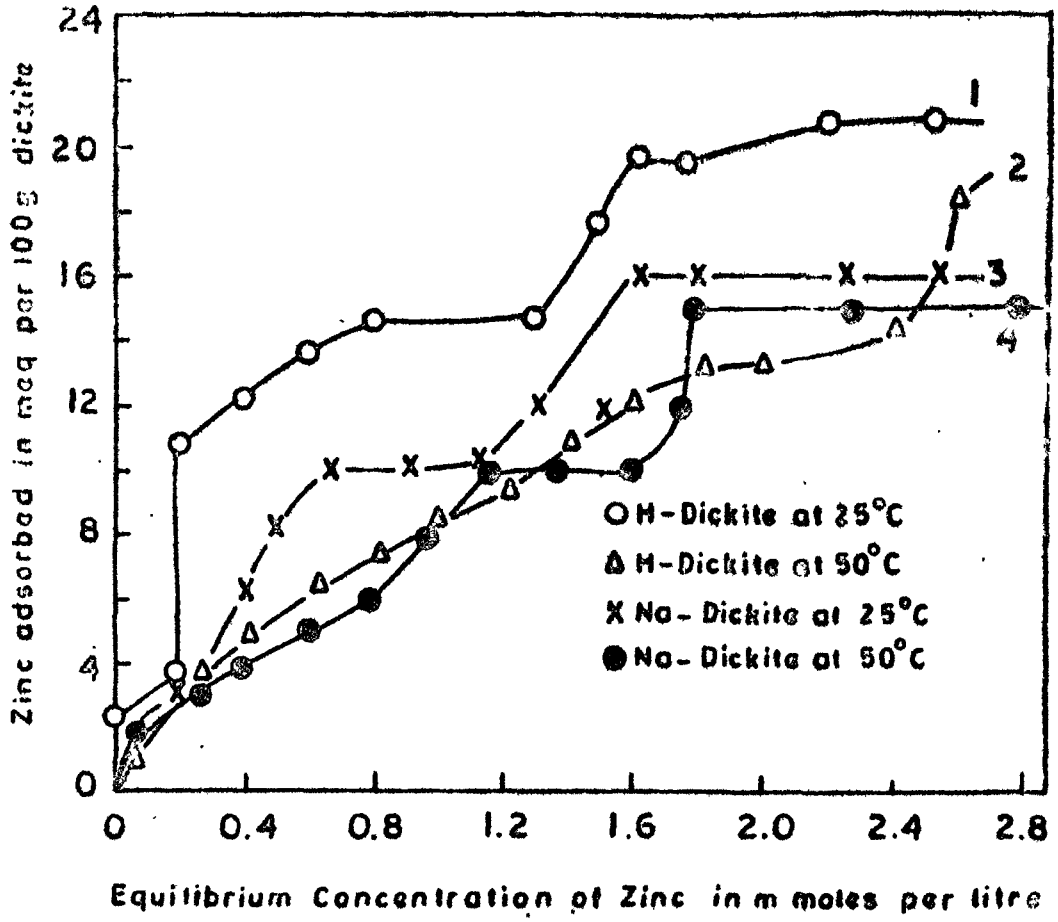

FIG. 8 ADSORPTION ISOTHERMS OF H- AND Na-DICKITE AT 25° AND 50°C

H-dickite at 25°C were vertical and could be resolved into two portions separated by a slope, both indicating rapid exchange adsorption till a limiting value as indicated by a long flat plateau was reached at a value somewhat higher than the CEC. An almost similar effect occurred during adsorption of zinc on Na-dickite with the long flat plateau being formed at the CEC. The two "H" portions indicated adsorption at two sites with different energy levels on H-dickite as advocated by Fordham[6]. When these sites were saturated, as indicated by the long plateau, new adsorption sites opened up due to the pressure of zinc ions producing a further rise with a change in the slope of the adsorption isotherms till it reached a constant value. These linear rising or "C" curves, both in the case of H-dickite and Na-dickite were due to slow penetration and fixation of zinc ions in the lattice micropores of the dickites. The results were in agreement with the observations of earlier workers[2] on the adsorption of zinc by clay minerals. The results also found support from the kinetic data discussed earlier in this communication which were indicative of two kinds of interactions during adsorption of zinc on dickites.

The isotherms at 50°C (Fig.8, curves 2 and 4), both in case of H-dickite and Na-dickite exhibited almost the same kind of behaviour except that at this temperature the initial "H" or high affinity portions were not so well formed. The initial adsorptive force at the higher temperature thus appeared to be lower. The curves also showed a decrease in adsorption with rise in temperature which was indicative of exothermic interactions. The average values of the rate constants for the Na-dickite system (table XVII) were

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2.25×10^3 min^{-1} at 25°C and 1.90×10^3 min^{-1} at 50°C respectively at a concentration of 140.0 meq. of zinc. The activation energy (ΔE) of adsorption of zinc over Na-clay was found to be 14.0 KCal $mole^{-1}$. Such a value could not be calculated in the case of adsorption of zinc on H-dickite due to uncertainty introduced by decomposition of H-clay with time at the higher temperature. A reference to Fig.8 (curves 1 and 3) further showed that inspite of a greater deflocculation effect and larger surface area exposed by Na-dickite, a greater amount of zinc was adsorbed by H-dickite than Na-dickite at the natural pH values (4.2 and 6.5 respectively) of the clays. The nature of exchangeable cation thus determined the order of adsorption, the order being H-dickite > Na-dickite at a pH value below 7.

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C H A P T E R - II

STUDIES ON THE THERMODYNAMICS OF EXCHANGE WITH CLAYS

PART I: Studies on the thermodynamics of exchange of nicotine with aluminium-montmorillonite.

PART II: Studies on the thermodynamics of zinc exchange with montmorillonite.

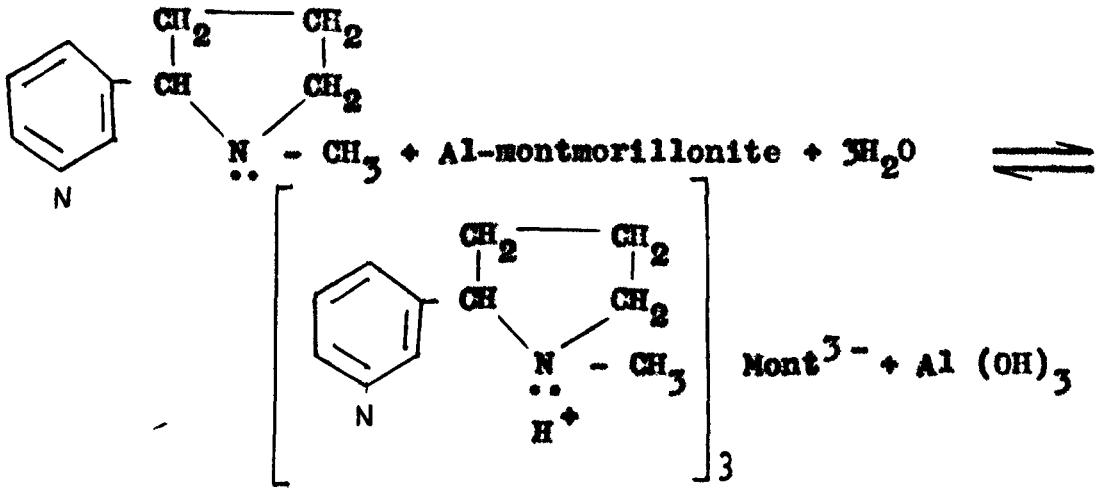
CHAPTER II, PART I

STUDIES ON THE THERMODYNAMICS OF EXCHANGE OF NICOTINE WITH ALUMINIUM-MONTMORILLONITE

I N T R O D U C T I O N

A study of the adsorption of pesticidal organic molecules plays an important part in understanding the mechanism of their interaction with soil clays. Nicotine is a powerful pesticide which has a vital influence on the functions of the central nervous system. It is a cationic molecule in which the aliphatic nitrogen of the pyrrolidine ring is the electron donor species.

Clays constitute the most important reactive surfaces of the soil. They provide sites for cation exchange and many other reactions and form clay-organic complexes. In their aluminium saturated form montmorillonite behaves as a Bronsted acid[1] to supply protons to nicotine in aqueous medium as has been shown for many amines. With nicotine it can undergo the following exchange reactions



Investigations in these laboratories revealed that the above reaction was reversible[2].

In the study of ion exchange it has been recognised that although the two ions may exchange stoichiometrically, they would not, in general, be held equally strongly by the exchanger. Preference by the exchanger plays an important role in ion exchange reactions. The importance of a study of the retention of complex pesticides such as nicotine on acid soils led us to investigate the interaction of nicotine on aluminium-montmorillonite with the help of exchange isotherms and thermodynamic parameters. The treatment is mostly based on the thermodynamic formulations of previous workers[3,4,5]. It has been felt that such a study will throw considerable light on the mechanism of nicotine adsorption and release on aluminium montmorillonite.

EXPERIMENTAL

The clay mineral used in these investigations was montmorillonite collected from Polkville, Mississippi (USA). The mineralogical composition of less than 2 u fraction was verified by x-ray diffraction and was found to consist of montmorillonite mainly. The mineral was broken up in a mortar using a rubber covered pestle. The organic matter was oxidised with hydrogen peroxide and the mixture diluted with distilled water. The clay was then dispersed by electrical stirring. Less than 2 μ clay fraction was obtained by centrifugation at a speed of 3500 rpm in the basket type "International Chemical" centrifuge.

PREPARATION OF SODIUM MONTMORILLONITE

The sodium montmorillonite suspension was prepared in the same manner as described earlier in Chapter I, Part I of this thesis in case of sodium dickite.

PREPARATION OF ALUMINIUM MONTMORILLONITE

A part of the above sodium saturated clay suspension was converted in aluminium saturated montmorillonite by saturating it repeatedly with 0.33M $AlCl_3$ at pH 3.2 and washing with deionized water to remove the excess salt.

DETERMINATION OF THE CONCENTRATION OF SUSPENSION

The concentration of aluminium-montmorillonite suspension was determined by evaporating 10 ml of the clay suspension in petri dish of known weight and drying the residue at 105°C in an oven and finally determining the constant weight of the residue. The concentrations of aluminium-montmorillonite suspension was 8.6 g per litre.

CATION EXCHANGE CAPACITY

The cation exchange capacity of aluminium-montmorillonite was determined by the method of Frink and Peech[6] in which 100 ml duplicate samples of 8.6 g per litre montmorillonite suspension were treated with 5 washes of 1N solution of $AlCl_3$. Following the saturation, the excess salt was removed from the aluminium-montmorillonite suspension by washing five times with 0.001N $AlCl_3$ solution and then with a little of 95% ethanol. The aluminium-

montmorillonite was then subjected to extraction with an acid salt mixture (0.1N HCl + 1N NaCl) followed by washing with 95% alcohol. The aluminium released was then determined spectrophotometrically at 520 mμ with aluminon as the colour reagent. The aluminium CEC was then calculated. It gave a value of 70 meq. per 100 g montmorillonite.

EXCHANGE EXPERIMENTS

For the exchange experiments the pH of the clay suspensions was adjusted to 5.1 with dilute HNO_3 to prevent the possibility of hydroxide precipitation. The exchange was carried out by taking 10 ml each of aluminium-montmorillonite clay suspension in several glass stoppered tubes, adding various concentrations of 0.03077M nicotine solution and adjusting the mixture to 25 ml with distilled water. The tubes were shaken for twelve hours at 30 ± 1°C in the first set of experiments and 60 ± 1°C in the second set of experiments in a thermostatic water bath to attain equilibrium. The mixtures were then centrifuged and the aluminium and nicotine estimated in the supernatant liquids as follows.

ESTIMATION OF ALUMINIUM

During the exchange experiments, the aluminium in the supernatant liquids was estimated colorimetrically by the method of Jackson[7] by taking 10 ml of buffer solution of pH = 4.2 in a number of 50 ml pyrex flasks, adding 20 ml of distilled water and 10 ml of 0.04 percent aluminon solution in each flask. To each of the flasks 5 ml of the supernatants containing exchanged aluminium

were added and the mixtures immediately diluted upto the mark (50 ml), and the contents well mixed. After 25 minutes the absorbance of the solutions were recorded at 520 mu with the help of Bausch and Lomb spectronic 20. A standard curve for aluminium in the range 0 to 50 µg in 50 ml of solution using same reagents as above was earlier prepared and is represented vide Fig.9. Aluminium content in the solutions was evaluated from the standard curve. The aluminium in the clay phase was obtained by difference (i.e., aluminium added minus aluminium in solution). The results at 30° and 60°C are recorded in tables XVIII and XIX.

ESTIMATION OF NICOTINE

For the estimation of nicotine, 5 ml portions of the supernatant liquids were taken in a number of beakers to which methyl red indicator was added in each beaker. The contents were then titrated with standard hydrochloric acid. From the volume of hydrochloric acid used up the amount of nicotine in solution phase was calculated. The nicotine in the clay phase was obtained by difference from nicotine added minus nicotine in the liquid phase. The results obtained are recorded in tables XX and XXI.

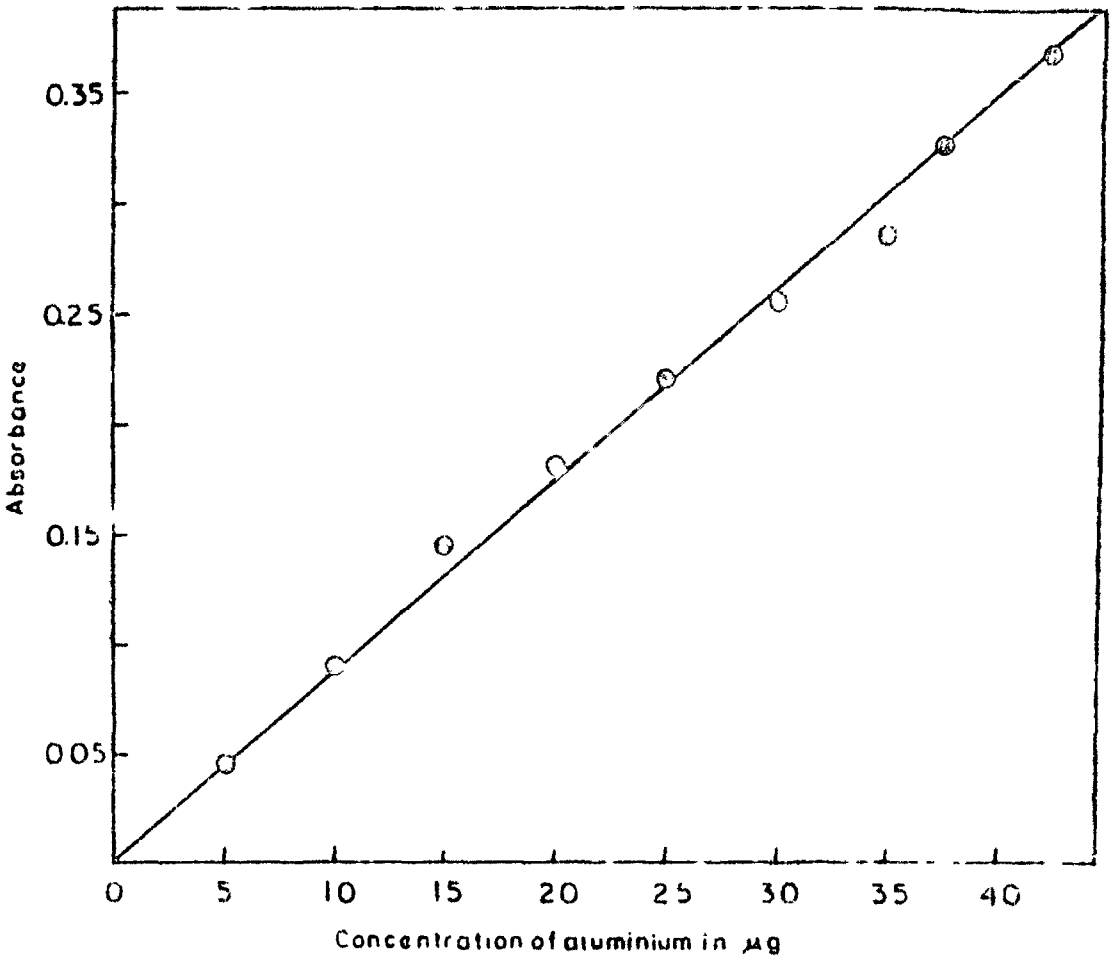


FIG 9 STANDARD CURVE OF ALUMINIUM WITH SPECTROPHOTOMETRY

TABLE XVIII

Estimation of aluminium spectrophotometrically in the equilibrium suspension during aluminium-nicotine exchange at 30°C

Concentration of aluminium-montmorillonite suspension = 8.6 g per litre

Volume of aluminium-montmorillonite suspension taken = 10.0 ml

Total volume of the mixture (clay suspension + nicotine + water) = 25.0 ml

Volume of supernatant liquid taken for estimating aluminium = 5.0 ml

Aluminium CEC of montmorillonite = 70 meq. per 100 g

Absorbance	Reading from standard curve	Aluminium in equilibrium suspension (in µg)	Meq. of aluminium per 100 g montmorillonite in the equilibrium suspension	Meq. of aluminium per 100 g montmorillonite in solid clay phase
0.065	7.50	37.50	4.85	65.15
0.070	7.75	38.75	5.00	65.00
0.070	8.00	40.00	5.16	64.84
0.075	8.55	42.75	5.52	64.48
0.080	9.10	45.50	5.86	64.14
0.090	10.03	51.50	6.65	63.35
0.095	11.10	55.60	7.19	62.81
0.105	12.00	60.00	7.74	62.26
0.120	13.70	68.60	8.87	61.13
0.130	14.90	74.50	9.62	60.38
0.145	16.50	82.50	10.65	59.35
0.180	20.50	102.50	13.24	56.76
0.200	22.70	113.60	14.69	55.31

TABLE XIX

Estimation of aluminium spectrophotometrically in the equilibrium suspension during aluminium nicotine exchange at 60°C

Concentration of aluminium-montmorillonite suspension = 8.6 g per litre

Volume of aluminium-montmorillonite suspension taken = 10.0 ml

Total volume of the mixture (clay suspension + nicotine + water) = 25.0 ml

Volume of supernatant liquid taken for estimating aluminium = 5.0 ml

Aluminium CEC of montmorillonite = 70 meq. per 100 g

Absorbance	Reading from standard curve	Aluminium in equilibrium suspension (in mg)	Meq. of aluminium per 100 g montmorillonite in the equilibrium suspension	Meq. of aluminium per 100 g montmorillonite in solid clay phase
0.065	7.75	38.70	5.00	65.00
0.075	8.70	43.50	5.60	64.40
0.085	9.50	47.40	6.12	63.88
0.090	10.20	51.10	6.61	63.39
0.100	11.20	56.00	7.22	62.78
0.120	13.70	68.50	8.86	61.14
0.145	16.80	84.00	10.86	59.14
0.190	22.00	110.00	14.20	55.80
0.210	24.00	120.00	15.50	54.51
0.245	28.10	140.50	18.15	51.85
0.270	31.00	150.00	20.01	49.99
0.320	36.75	183.70	23.73	46.27
0.350	40.20	201.10	25.99	44.01

TABLE XX

Estimation of nicotine volumetrically in the equilibrium suspension during aluminium nicotine exchange at 30°C

Concentration of aluminium montmorillonite suspension = 8.6 g per litre

Volume of aluminium montmorillonite suspension = 10.0 ml

Strength of nicotine solution = 0.03077M

Total volume of the mixture = 25.0 ml

Volume of nicotine added in ml	Volume in ml of 0.03077M HCl used in titration of nicotine	Meq. of nicotine added per 100 g clay	Meq. of nicotine left in the equilibrium suspension	Meq. of nicotine adsorbed per 100 g clay
0.00	0.00	0.00	0.00	0.00
0.13	0.03	4.48	0.90	3.58
0.25	0.05	8.95	1.80	7.15
0.50	0.10	17.90	3.58	14.32
1.00	0.20	35.80	7.16	28.64
1.50	0.30	53.70	10.74	42.96
2.00	0.40	71.60	14.32	57.28
2.50	0.50	89.50	17.90	71.60
3.00	1.00	107.40	35.80	71.60
4.00	1.80	143.20	64.44	78.76
5.00	2.70	179.00	96.60	82.40
6.00	3.50	214.80	125.30	89.50
7.00	4.30	250.60	153.94	96.66
8.00	4.55	286.40	163.00	123.40

TABLE XXI

Estimation of nicotine volumetrically in the equilibrium suspension during aluminium nicotine exchange at 60°C

Concentration of aluminium montmorillonite suspension = 8.6 g per litre

Volume of aluminium montmorillonite suspension = 10.0 ml

Strength of nicotine solution = 0.03077M

Total volume of the mixture = 25.0 ml

Volume of nicotine added in ml	Volume in ml of 0.03077M HCl used in titration of nicotine	Meq. of nicotine added per 100 g clay	Meq. of nicotine left in the equilibrium suspension	Meq. of nicotine adsorbed per 100 g clay
0.00	0.00	0.00	0.00	0.00
0.13	0.03	4.48	0.88	3.60
0.25	0.05	8.95	1.78	7.17
0.50	0.10	17.90	3.58	14.32
1.00	0.20	35.80	7.16	28.64
1.50	0.30	53.70	10.74	42.96
2.00	0.40	71.60	14.32	57.28
2.50	1.11	89.50	32.22	57.29
3.00	1.60	107.40	57.28	50.12
4.00	2.20	143.20	78.76	64.44
5.00	3.00	179.00	107.40	71.60
6.00	4.09	214.80	146.50	68.28
7.00	4.90	250.60	175.42	75.18
8.00	5.46	286.40	195.40	91.00

RESULTS AND DISCUSSION

The exchange reaction between nicotine and aluminium-montmorillonite in dilute suspensions can be described by the equation:

$$\bar{C}_{Al} + C_{nicotine} \rightleftharpoons C_{Al} + \bar{C}_{nicotine} \quad \ldots\ldots (1)$$

The barred quantities refer to the equivalent concentrations of the ion concerned in the clay phase and the unbarred, the concentrations in the solution. The equivalent ionic fractions of nicotine and aluminium in montmorillonite and in the solution were calculated from the expressions

$$\bar{X}_{nicotine} = \frac{\bar{C}_{nicotine}}{\bar{C}}, \quad X_{nicotine} = \frac{C_{nicotine}}{C}$$

$\bar{X}_{Al} = \frac{\bar{C}_{Al}}{\bar{C}}$ and $X_{Al} = \frac{C_{Al}}{C}$, where $\bar{C}$ and C were the total concentrations in the clay and solution phases respectively. The values obtained both at 30° and 60°C are in tables XXII and XXIII. A plot of the results gave isotherms given in Fig.10. The deviation of the isotherms from the diagonal indicated a strong preference by montmorillonite for aluminium as compared to nicotine at both the temperatures in the entire range of concentration studied.

The affinity of montmorillonite for nicotine was further examined by the separation factor

$$\alpha^{nicotine}_{Al} = \frac{\bar{X}_{nicotine}}{\bar{X}_{Al}} \frac{X_{Al}}{X_{nicotine}} \quad \ldots\ldots (2)$$

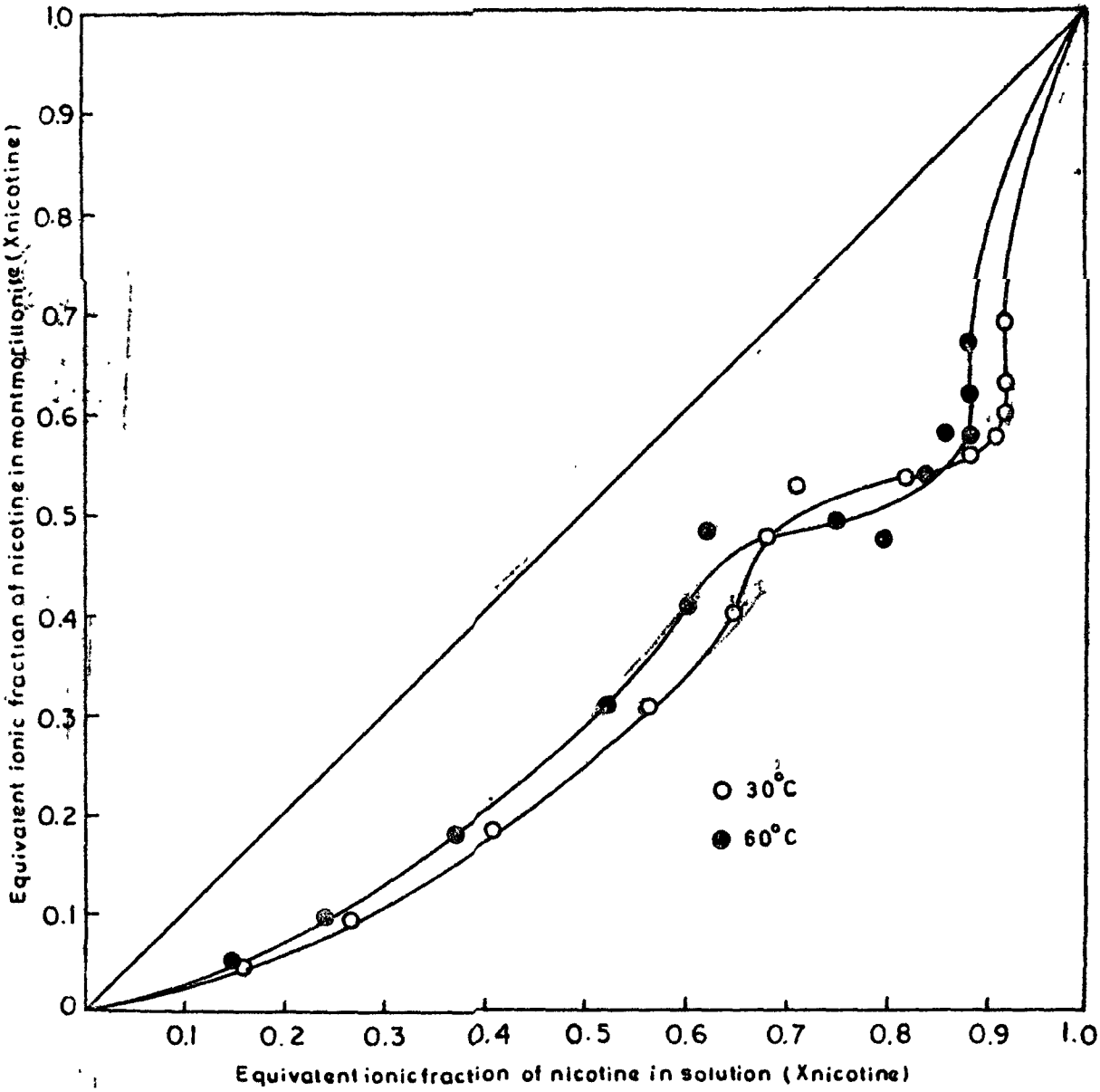


FIG. 10 EXCHANGE ISOTHERMS OF NICOTINE ON AL-MONTMORILLONITE AT DIFFERENT TEMPERATURES

TABLE XXII

Values of equivalent ionic fractions of aluminium, nicotine, separation factor and selectivity quotient at 30°C for the nicotine exchange on aluminium montmorillonite

$\bar{X}_{Al}$	X_{Al}	$\bar{X}_{Nicotine}$	$X_{Nicotine}$	$\alpha^{Nicotine}_{Al}$	K_C	Log K_C
0.948	0.843	0.052	0.156	0.296	0.0234	- 1.631
0.901	0.735	0.099	0.265	0.305	0.0438	- 1.460
0.819	0.590	0.181	0.410	0.318	0.0616	- 1.210
0.692	0.435	0.307	0.565	0.342	0.1007	- 0.997
0.599	0.353	0.401	0.647	0.365	0.1403	- 0.853
0.525	0.317	0.475	0.683	0.420	0.2031	- 0.692
0.467	0.286	0.533	0.713	0.458	0.2557	- 0.592
0.465	0.178	0.535	0.822	0.249	0.1055	- 0.977
0.437	0.121	0.563	0.879	0.177	0.0727	- 1.139
0.423	0.090	0.577	0.909	0.135	0.0544	- 1.264
0.399	0.078	0.601	0.922	0.127	0.0541	- 1.267
0.370	0.079	0.630	0.921	0.146	0.0683	- 1.166
0.309	0.083	0.690	0.917	0.202	0.1144	- 0.942

TABLE XXIII

Values of equivalent ionic fractions of aluminium, nicotine, separation factor and selectivity quotient at 60°C for the nicotine exchange on aluminium montmorillonite

$\bar{X}_{Al}$	X_{Al}	$\bar{X}_{Nicotine}$	$X_{Nicotine}$	$\alpha^{Nicotine}_{Al}$	K_C	log K_C
0.947	0.850	0.052	0.150	0.311	0.0263	- 1.580
0.900	0.759	0.100	0.241	0.349	0.0602	- 1.220
0.817	0.631	0.187	0.369	0.391	0.1000	- 1.000
0.689	0.480	0.311	0.520	0.417	0.1491	- 0.827
0.594	0.402	0.406	0.598	0.459	0.2119	- 0.674
0.516	0.382	0.484	0.618	0.580	0.3557	- 0.449
0.508	0.252	0.492	0.748	0.362	0.1411	- 0.851
0.527	0.199	0.473	0.801	0.223	0.0777	- 1.110
0.458	0.164	0.542	0.836	0.232	0.0975	- 1.011
0.420	0.144	0.580	0.855	0.233	0.1070	- 0.971
0.423	0.120	0.577	0.880	0.186	0.0799	- 1.098
0.381	0.119	0.619	0.881	0.219	0.1083	- 0.965
0.326	0.117	0.674	0.883	0.274	0.1596	- 0.797

Values lower than unity (Tables XXII and XXIII) at both the temperatures indicated a higher preference by montmorillonite for trivalent aluminium than for the organic ion. However, the preference for nicotine as indicated by the separation factor increased with an increase in its concentration upto a certain limit of $X_{nicotine}$ after which it declined again. The separation factor was also larger at higher temperature (Tables XXII and XXIII) indicating an increase in the preference for nicotine with rise in temperature.

Taking the ratio of activity coefficients as unity[8] in the dilute range of concentration studied, the selectivity coefficients at various values $\bar{X}_{nicotine}$ were calculated from the expression[9]

$$K_C = \frac{\left(\bar{X}_{nicotine}\right)^3 \left(X_{Al}\right)}{\left(\bar{X}_{Al}\right) \left(X_{nicotine}\right)^3} \qquad \ldots\ldots\ldots (3)$$

A plot of the values of K_C at 30° and 60°C is given in Fig.11.

For a further study of the affinity, the thermodynamic equilibrium constant K was calculated from the relationship

$$\ln K = \left(Z_A - Z_B\right) \int_0^1 \ln K_C \, d\bar{X}_{nicotine} \qquad \ldots\ldots (4)$$

where Z_A and Z_B were the charges on the competing ions. The integral was evaluated from the areas under the curves (Fig.11) using the trapezoidal rule. The value of K at 30°C was lower than at 60°C indicating that nicotine had a higher preference for montmorillonite at the higher temperature[10].

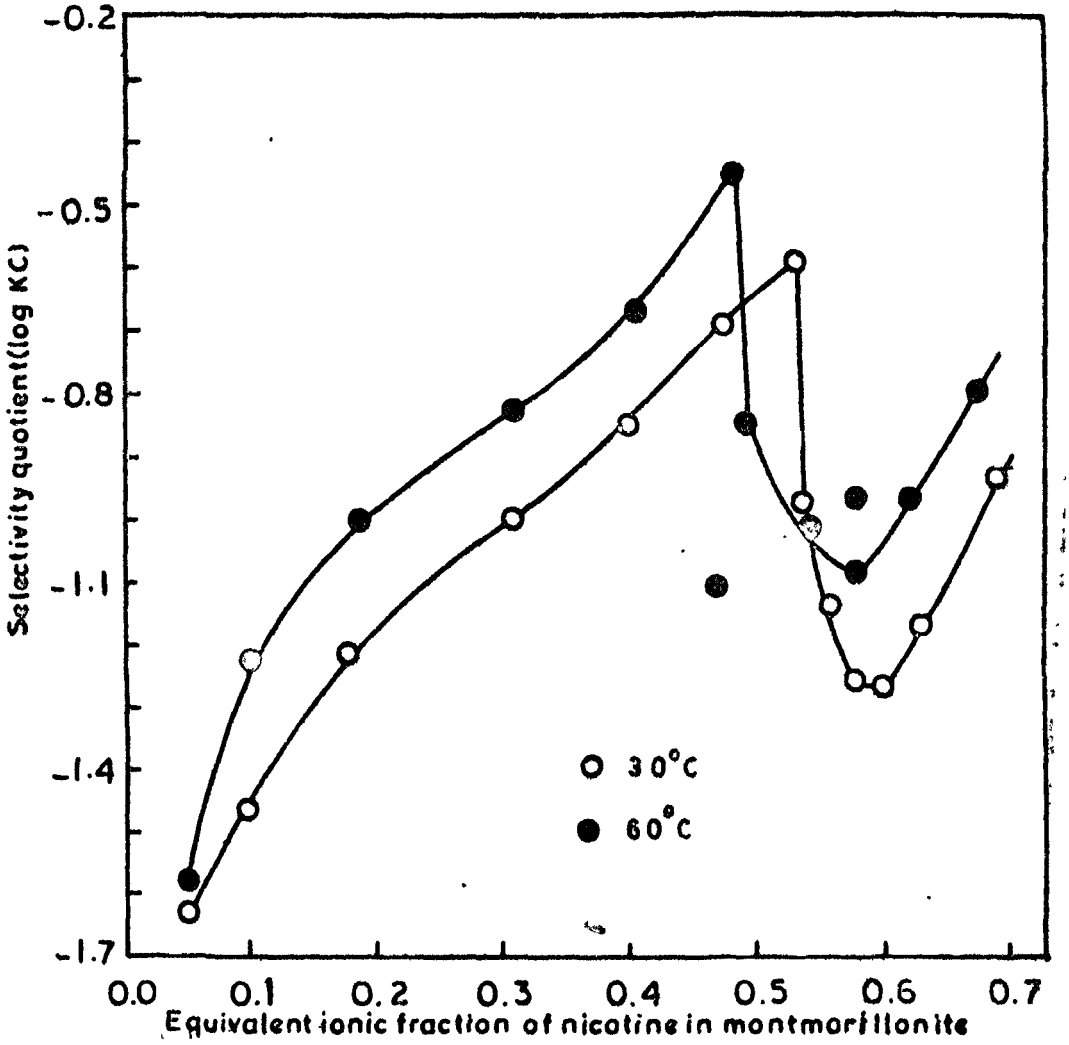


FIG. 11 LOGARITHMS OF SELECTIVITY QUOTIENTS VS. EQUIVALENT IONIC FRACTION OF NICOTINE IN MONTMORILLONITE

The Gibbs free energy for the interaction was obtained by the equation

$$\Delta G^{\circ} = - RT \ln K \qquad \ldots\ldots\ldots\ldots (5)$$

The negative value of free energy implied a higher preference for nicotine. That was, however, not conclusive because formation of nicotinium clay was accompanied by an increase in enthalpy pointing to a stronger binding of aluminium.

The standard enthalpy change was calculated from the van't Hoff isochore

$$\ln \left(\frac{K_{T_2}}{K_{T_1}} \right) = - \frac{\Delta H^{\circ}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \qquad \ldots\ldots\ldots (6)$$

and the standard entropy change by the equation

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$$

The values are given in table XXIV which indicated that the interaction was affected both by enthalpy and entropy effects. The positive value of enthalpy suggested temperature dependent adsorption and that nicotine was less strongly bound on the montmorillonite surface than aluminium. Entropy gain accompanying nicotine adsorption further justified this assumption. It indicated a more extended diffused and disordered arrangement of nicotinium ions in the Gouy layer with aluminium forming a more ordered arrangement in the Stern layer. Valence, electrostatic considerations and the smaller size of aluminium ions as compared to the nicotinium ions justified the conclusion.

TABLE XXIV

Thermodynamic values for the nicotine exchange with aluminium montmorillonite at 30° and 60°C

Thermodynamic parameters	Values at 30°C	Values at 60°C
K	1.51	1.90
ΔG° (cal/moles)	-247	-424
ΔH° (cal/moles)	1539	
ΔS° (cal/moles)	5.89	5.89

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CHAPTER - II, PART - II

STUDIES ON THE THERMODYNAMICS OF ZINC EXCHANGE WITH MONTMORILLONITE

I N T R O D U C T I O N

Zinc formulations are being extensively used as pesticides. Zinc is also an important micronutrient. The adsorption of zinc and its reactions with clays and soils are therefore receiving increasing attention. Zinc deficiencies are common in plants growing on sodic soils. Increasing applications of its pesticides may result in accumulation of zinc and gradual release from soils. The process of ion exchange is important in this direction. The cation exchange of zinc on montmorillonite as well as its exchange adsorption on soils have been studied by several workers[1,2]. In the study of ion exchange it has been noticed that although two ions may exchange stoichiometrically, they would not, in general, be preferred or bound equally strongly on a surface. In view of the importance of the nature of ion exchange, the exchange of zinc with Na-montmorillonite has been studied with the help of thermodynamic models[3,4,5]. It has been felt that such a study will be of considerable significance in understanding the mechanism of zinc interaction with Na-montmorillonite, a clay mineral which occurs widely in montmorillonitic sodic soils.

E X P E R I M E N T A L

The clay mineral used in these studies was montmorillonite extracted from a Mississippi bentonite which was obtained from

Ward's Natural Science Establishment, Rochester, New York. The bentonite was then dispersed by electrical stirring. Less than 2 μ montmorillonite fraction was obtained by centrifugation at a speed of 3500 rpm in the "International Chemical" centrifuge.

PREPARATION OF SODIUM MONTMORILLONITE

Sodium saturated montmorillonite was prepared from the above montmorillonite as described earlier in Chapter I, Part I of this thesis.

DETERMINATION OF CONCENTRATION OF MONTMORILLONITE SUSPENSION

The concentration of sodium montmorillonite suspension was determined by evaporating 10 ml of the clay suspension in petri dish of known weight and drying the residue at 105°C in an oven and finally determining the constant weight of the residue. The concentration of sodium montmorillonite suspensions varied from 14.6 to 15.3 g per litre.

CATION EXCHANGE CAPACITY

The cation exchange capacity of Na-montmorillonite was determined by ammonium acetate method of Jackson[6]. For this purpose 10 ml of the clay suspension was taken in 50 ml centrifuge tube, and treated with 30 ml of sodium acetate solution. The tube was shaken for 5 minutes on electrical shaker and the mixture centrifuged. The supernatant liquid was decanted and this procedure repeated four times with fresh portion of the acetate solution. After this treatment 30 ml of 95% ethanol was added in the tube and the tube

shaken for five minutes and the contents centrifuged. The clay suspension was then extracted by adding three 30 ml portions of ammonium acetate solution, the mixture was then centrifuged and the extract collected. Sodium was then determined in the extract by flame photometer. The value of CEC as calculated came out to be 70 meq. per 100 g clay.

EFFECT OF TIME ON THE EXCHANGE OF ZINC

For determination of time of exchange equilibrium at constant ionic strength three sets of 10 ml suspensions of Na-montmorillonite were treated with 1, 6 and 15 ml of 0.02N $Zn(NO_3)_2$ and 14, 9 and 0 ml of 0.03N $NaNO_3$ solutions respectively. The mixtures were shaken for 1 hour. Similar exchanges were carried out at 3, 6 and 9 hours also. At the end of the above specified time intervals the mixtures were centrifuged and zinc estimated in the supernatant liquids by titration with a standard solution of EDTA as described in Chapter I, Part II of this thesis. The amount of zinc exchanged at different time intervals was then obtained from the amount of zinc added minus zinc remaining in the supernatants. The results are illustrated by Fig.12, curves 1-3 and represented vide table XXV. A time of 3 hours was found to be sufficient for attainment of equilibrium during the exchange.

EFFECT OF pH ON EXCHANGE OF ZINC

Cation exchange in clays is also controlled by pH. For determination of pH suitable to carry out exchange studies, two sets of 10 ml suspensions of Na-montmorillonite were treated with

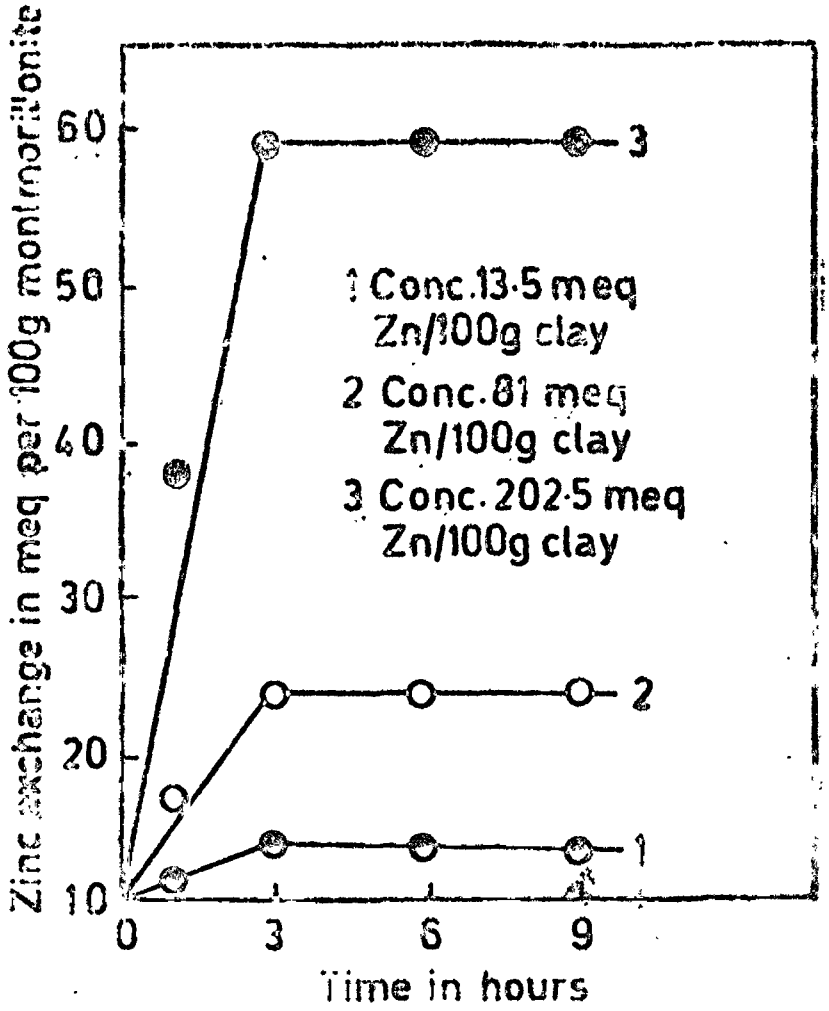


FIG.12 EFFECT OF TIME ON THE ADSORPTION OF ZINC BY SODIUM MONTMORILLONITE AT 30° C

0.1N HNO_3 and 0.1N NaOH to obtain the desired levels of pH (3, 4, 5, 6 and 7 approximately). Zinc exchange was then carried out at a constant ionic strength by shaking the mixtures with variable and required volumes of $Zn(NO_3)_2$ and Na-montmorillonite at a temperature of 30°C and a time of 3 hours. The results of the pH effect on exchange are recorded in Fig.13, curves 1-2 and represented vide table XXVI.

EXCHANGE EXPERIMENTS

Since exchange of zinc with Na-montmorillonite was found to be unaffected by variation of pH from 4.5 to 6, the exchange isotherms were determined at pH = 5.0. This also avoided hydroxide precipitation. For the exchange experiments 10 ml samples of Na-montmorillonite were taken in a large number of glass stoppered tubes and their pH adjusted to 5.0 by adding 0.1N HNO_3. The suspensions were then treated with various but proportionate amounts of 0.02N $Zn(NO_3)_2$ and 0.03N $NaNO_3$ to provide a constant ionic strength and a constant volume (25 ml) for the exchange. The tubes were shaken at 30 ± 0.1°C in the first set of experiments and 60 ± 0.1°C in the second set for 3 hours in a thermostatic water bath. The mixtures were then immediately centrifuged and sodium and zinc estimated in the supernatants by flame photometry (as below) and titration with a standard solution of EDTA, respectively. The corresponding concentration of sodium in the clay phase was obtained by substraction of sodium concentration in the supernatant or equilibrium suspension from sodium added for adjustment of ionic strength plus Na-CEC. Similarly the amount of zinc taken up by the clay surface in

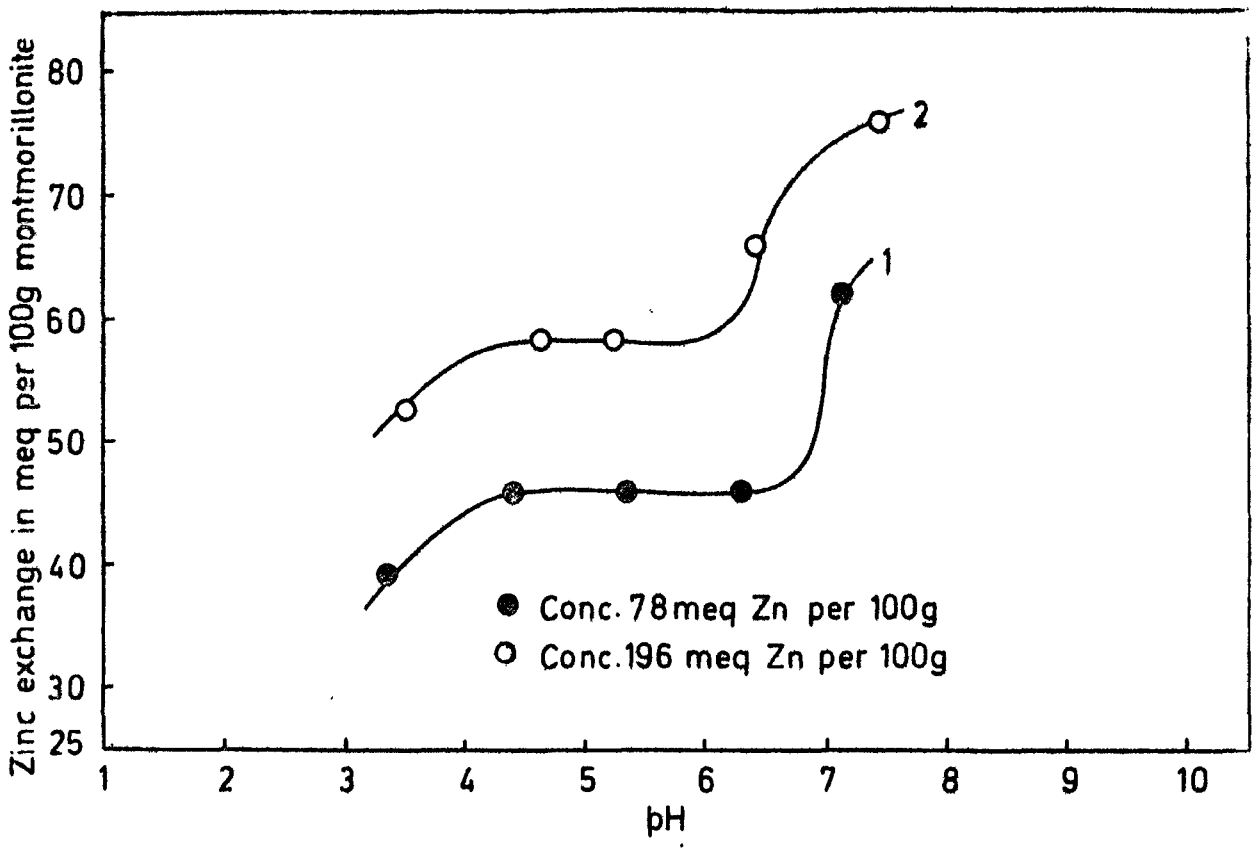
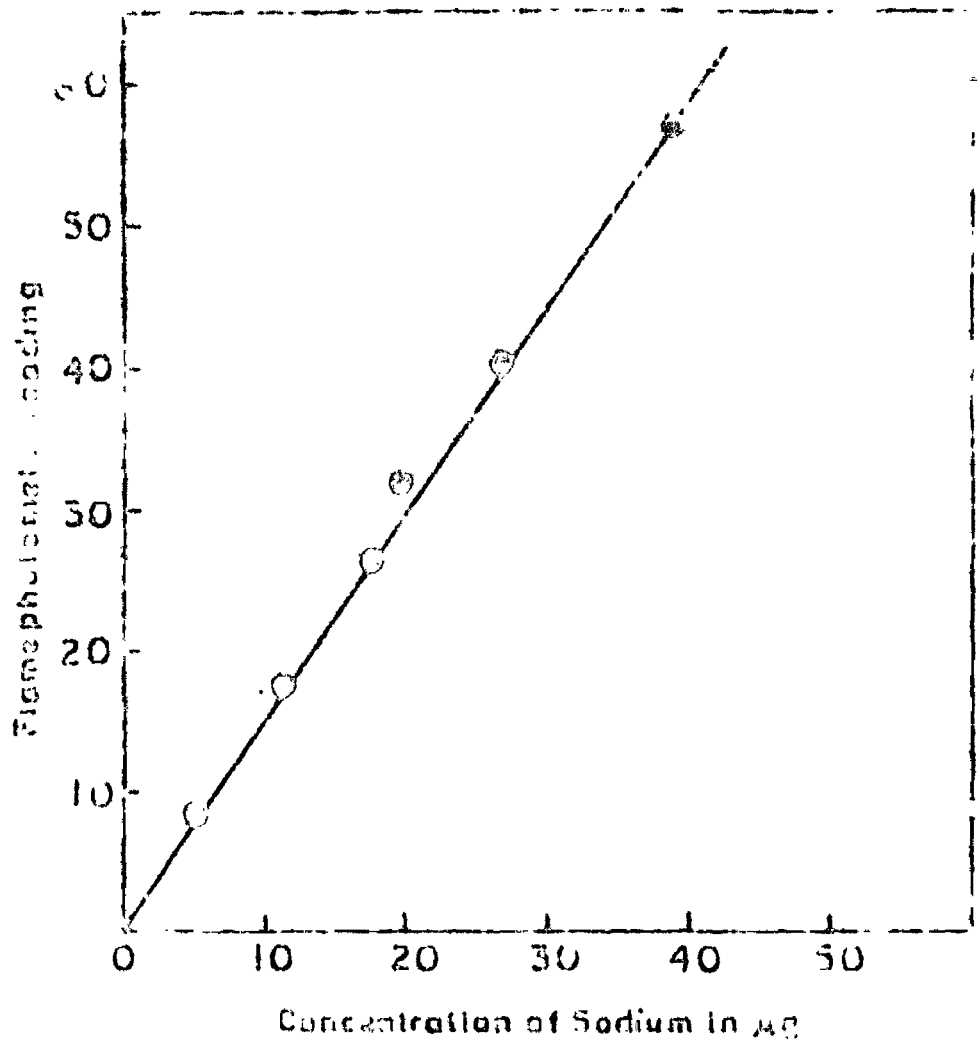


FIG.13 EFFECT OF pH ON THE ADSORPTION OF ZINC BY Na–MONTMORILLONITE AT 30° C

replacing sodium was obtained by difference between the amount of zinc added and the amount of zinc left behind in the equilibrium suspension. The results obtained for zinc at 30° and 60°C are recorded in tables XXVII to XXVIII.

DETERMINATION OF SODIUM BY FLAME PHOTOMETRY

For the estimation of sodium in the equilibrium suspension, a standard curve (Fig.14) was first prepared by taking 25 ml standards of 0 to 50 ug of sodium. For the estimation of sodium in 25 ml clay suspension, 1 ml of the supernatant liquid from the exchange experiment was diluted to 100 ml. 10 ml of this solution was further diluted to 25 ml and reading taken over the flame photometer using sodium filter. The concentration of sodium in the equilibrium suspension was then obtained with the help of the standard curve. From the concentration of sodium in the equilibrium suspension, its concentration in the montmorillonite phase was obtained by difference as described earlier. The results are given in tables XXIX and XXX.



STANDARD CURVE OF SODIUM WITH
FLAME PHOTOMETER

TABLE XXV

Effect of time on exchange of zinc by sodium saturated montmorillonite at 30°C at constant ionic strength

Concentration of sodium montmorillonite suspension = 14.8 g per litre

Volume of sodium montmorillonite taken = 10.0 ml

Strength of zinc nitrate solution = 0.02N

Total volume of the mixture = 25.0 ml

Experiment No.	Time in hours	Meq.of zinc added per 100 g clay	Volume of 0.02N EDTA used for titration	Meq.of zinc in equilibrium suspension per 100 g clay	Meq.of zinc exchanged per 100 g clay
1	1	13.5	0.18	2.4	11.1
	3	13.5	0.00	0.0	13.5
	6	13.5	0.00	0.0	13.5
	9	13.5	0.00	0.0	13.5
2	1	81.0	4.78	64.5	16.5
	3	81.0	4.26	57.5	23.5
	6	81.0	4.26	57.5	23.5
	9	81.0	4.26	57.5	23.5
3	1	202.5	12.22	165.0	37.5
	3	202.5	10.63	143.5	59.0
	6	202.5	10.63	143.5	59.0
	9	202.5	10.63	143.5	59.0

TABLE XXVI

Effect of pH on exchange of zinc by sodium saturated montmorillonite at 30°C

Concentration of sodium montmorillonite suspension = 15.3 g per lite

Volume of sodium montmorillonite taken = 10.0 ml

Strength of zinc nitrate solution = 0.02N

Total volume of mixture = 25.0 ml

Experiment No.	pH of the suspension	Meq.of zinc added per 100 g clay	Volume of 0.02N EDTA used for titration	Meq. of zinc in equilibrium suspension per 100 g clay	Meq.of zinc exchanged per 100 g clay
	3.35	78	2.97	38.8	39.2
	4.40	78	2.47	32.3	45.7
1	5.35	78	2.47	32.3	45.7
	6.30	78	2.47	32.3	45.7
	7.15	78	1.22	15.9	62.1
	3.50	196	11.00	143.7	52.3
	4.60	196	10.50	137.2	58.8
2	5.25	196	10.50	137.2	58.8
	6.50	196	10.00	130.7	65.3
	7.45	196	9.25	120.9	75.1

TABLE XXVII

Estimation of zinc in the equilibrium suspension during sodium zinc exchange at 30°C at constant ionic strength

Concentration of sodium montmorillonite suspension = 14.6 g per litre

Volume of sodium montmorillonite suspension taken = 10.0 ml

Total volume of the mixture = 25.0 ml

Meq. of zinc added per 100 g clay	Volume of 0.02N EDTA used for titration of zinc	Meq. of zinc in the equilibrium suspension	Molality of zinc in equilibrium suspension	Meq. of zinc adsorbed per 100 g clay
0.00	0.00	0.00	0.0000	0.00
6.85	0.20	2.74	0.0001	4.11
13.70	0.63	8.63	0.0003	5.10
20.55	1.00	13.70	0.0004	6.85
27.40	1.25	17.13	0.0005	10.27
54.80	1.88	25.76	0.0007	29.10
82.00	3.13	42.88	0.0012	39.40
109.60	5.00	68.50	0.0021	41.10
137.00	6.72	92.06	0.0026	45.00
164.70	8.20	112.34	0.0033	52.00
205.50	9.88	135.30	0.0040	70.20

TABLE XXVIII

Estimation of zinc in the equilibrium suspension during sodium zinc exchange at 60°C at constant ionic strength

Concentration of sodium montmorillonite suspension = 14.6 g per litre

Volume of sodium montmorillonite suspension taken = 10.0 ml

Total volume of the mixture = 25.0 ml

Meq. of zinc added per 100 g clay	Volume of 0.02N EDTA used for titration of zinc	Meq. of zinc in the equilibrium suspension	Molality of zinc in equilibrium suspension	Meq. of zinc adsorbed per 100 g clay
0.00	0.00	0.00	0.0000	0.00
6.85	0.20	2.74	0.0001	4.11
13.70	0.65	8.90	0.0003	4.80
20.55	1.10	15.07	0.0004	5.48
27.40	1.40	19.18	0.0006	8.22
54.80	2.50	34.25	0.0010	20.54
82.20	3.75	51.38	0.0015	30.82
109.60	5.60	76.72	0.0022	32.86
137.00	7.19	98.50	0.0029	38.50
164.70	9.10	124.67	0.0036	40.00
205.50	10.61	145.36	0.0042	60.14

TABLE XXIX

Estimation of sodium by flame photometry in the equilibrium suspension during sodium zinc exchange at 30°C at constant ionic strength

Concentration of sodium montmorillonite suspension = 14.6 g per litre

Volume of sodium montmorillonite suspension taken = 10.0 ml

Strength of sodium nitrate solution used for adjusting ionic strength = 0.03N

Total volume of mixture = 25.0 ml

BEC of Na-montmorillonite = 70 meq. per 100 g clay

Flame photometer reading	Sodium from standard curve (µg)	Total µg of sodium in equilibrium suspension	Meq. of sodium in equilibrium suspension	Meq. of sodium adsorbed per 100 g clay	Molality of sodium in equilibrium suspension
60	40.6	10150	302.3	65.7	0.0176
57	39.6	9900	294.8	62.9	0.0172
56	39.0	9750	290.4	56.9	0.0169
55	38.4	9600	285.9	51.3	0.0167
53	33.6	8400	250.2	45.9	0.0146
42	28.6	7150	212.9	42.1	0.0124
34	23.2	5800	172.9	41.0	0.0108
26	18.0	4500	134.0	35.1	0.0078
19	13.2	3300	98.3	28.0	0.0057
7	4.4	1100	32.8	13.1	0.0019

TABLE XXX

Estimation of sodium by flame photometry in the equilibrium suspension during sodium zinc exchange at 60°C at constant ionic strength

Concentration of sodium montmorillonite suspension = 14.6 g per litre

Volume of sodium montmorillonite suspension taken = 10.0 ml

Strength of sodium nitrate solution used for adjusting ionic strength = 0.03N

Total volume of mixture = 25.0 ml

DEC of Na-montmorillonite = 70 meq. per 100 g clay

Flame photometer reading	Sodium from standard curve (µg)	Total µg of sodium in equilibrium suspension	Meq. of sodium in equilibrium suspension	Meq. of sodium adsorbed per 100 g clay	Molality of sodium in equilibrium suspension
60	40.8	10200	303.8	64.2	0.0177
58	40.0	10000	297.8	59.9	0.0173
57	39.6	9900	294.9	52.4	0.0172
56	38.6	9650	287.4	49.8	0.0167
54	34.4	8600	256.0	40.9	0.0149
43	29.2	7300	216.4	38.6	0.0126
35	23.6	5900	175.7	38.2	0.0102
27	18.4	4600	137.0	32.2	0.0080
18	12.0	3000	104.2	26.3	0.0052
6	4.0	1000	29.8	12.8	0.0017

RESULTS AND DISCUSSION

The reaction between zinc ions in solution and sodium ions on the montmorillonite surface can be represented by the equation:

$$\bar{C}_{Na} + C_{Zn} \rightleftharpoons C_{Na} + \bar{C}_{Zn} \qquad \ldots\ldots\ldots \quad (1)$$

The concentrations of the ions concerned, in terms of equivalent ionic fractions, were calculated from the following expressions:

$$\bar{X}_{Zn} = \frac{\bar{C}_{Zn}}{\bar{C}}, \quad X_{Zn} = \frac{C_{Zn}}{C}, \quad \bar{X}_{Na} = \frac{\bar{C}_{Na}}{\bar{C}} \text{ and } X_{Na} = \frac{C_{Na}}{C},$$

where $\bar{C}$ was the total ion concentration in the clay phase and C that in the solution. The values obtained for the equivalent ionic fractions at 30° and 60°C were plotted and the exchange isotherms obtained are given in Fig.15.

Isotherms at both the temperatures were found to deviate from the diagonal indicating that a constant ionic strength zinc continuously replaced sodium from the montmorillonite surface over the entire range of concentrations studied by us and that it had a higher preference for the clay surface than sodium. The preference also varied with temperature, being higher at 30° than at 60°C.

For a further examination of the exchange behaviour in dilute montmorillonite suspension, the separation factors and selectivity coefficients[7] were calculated from the following respective expressions

$$\alpha^{Zn}_{Na} = \left(\frac{\bar{X}_{Zn}}{\bar{X}_{Na}}\right)\left(\frac{X_{Na}}{X_{Zn}}\right) \qquad \ldots\ldots\ldots \quad (2)$$

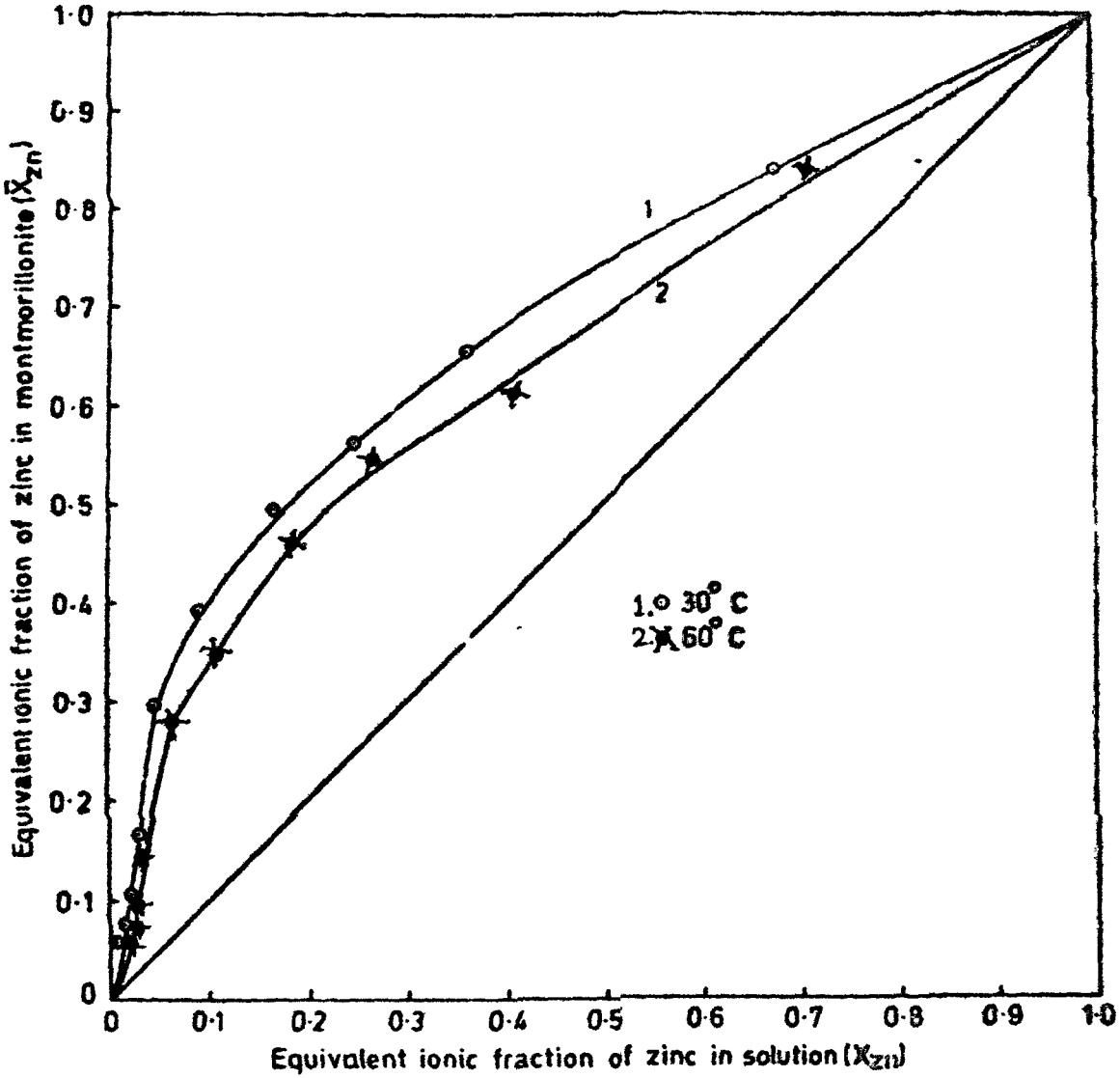


FIG.15 EXCHANGE ISOTHERMS FOR ZINC ION ON Na–MONTMORILLONITE.

Correcting the separation factor for interactions in the solution phase by introducing the factor γ_{Na}/γ_{Zn} we have

$$K_C = \frac{(\bar{X}_{Zn})}{(\bar{X}_{Na})^2} \quad \frac{(X_{Na}\gamma_{Na})^2}{(X_{Zn}\gamma_{Zn})} \qquad \ldots\ldots\ldots (3)$$

where γ_{Na} and γ_{Zn} were the activity coefficients of the two ions in the solution phase. The values are given in tables XXXI and XXXII. A plot of the effect of zinc concentration on selectivity coefficients is represented vide Fig.16. During the exchange, the selectivity quotient initially decreased, followed by a rise and then a fall at both the temperatures. Such a variation was indicative of significant interactions between zinc and Na-montmorillonite, the preference of zinc for the solid surface varying according to the nature of the curves (Fig.16).

For a further examination of the equilibria, the thermodynamic equilibrium constant K was calculated from the simplified relationship[3]

$$\ln K = (Z_B - Z_A) + \int_0^1 \ln K_C \, d\bar{X}_{Zn} \qquad \ldots\ldots (4)$$

where Z_A was the valence of sodium and Z_B of zinc. For the derivation of the above simplified formula from Gaines original relationship it became necessary to assume that $\int_B^{Z_A} (b) = \int_A^{Z_B} (a)$, namely that the activity of water was constant. That this was so borne out by the fact that the equilibria was carried out in dilute suspensions with a constant volume of water in the mixture.

The values of K were obtained by evaluating the integral

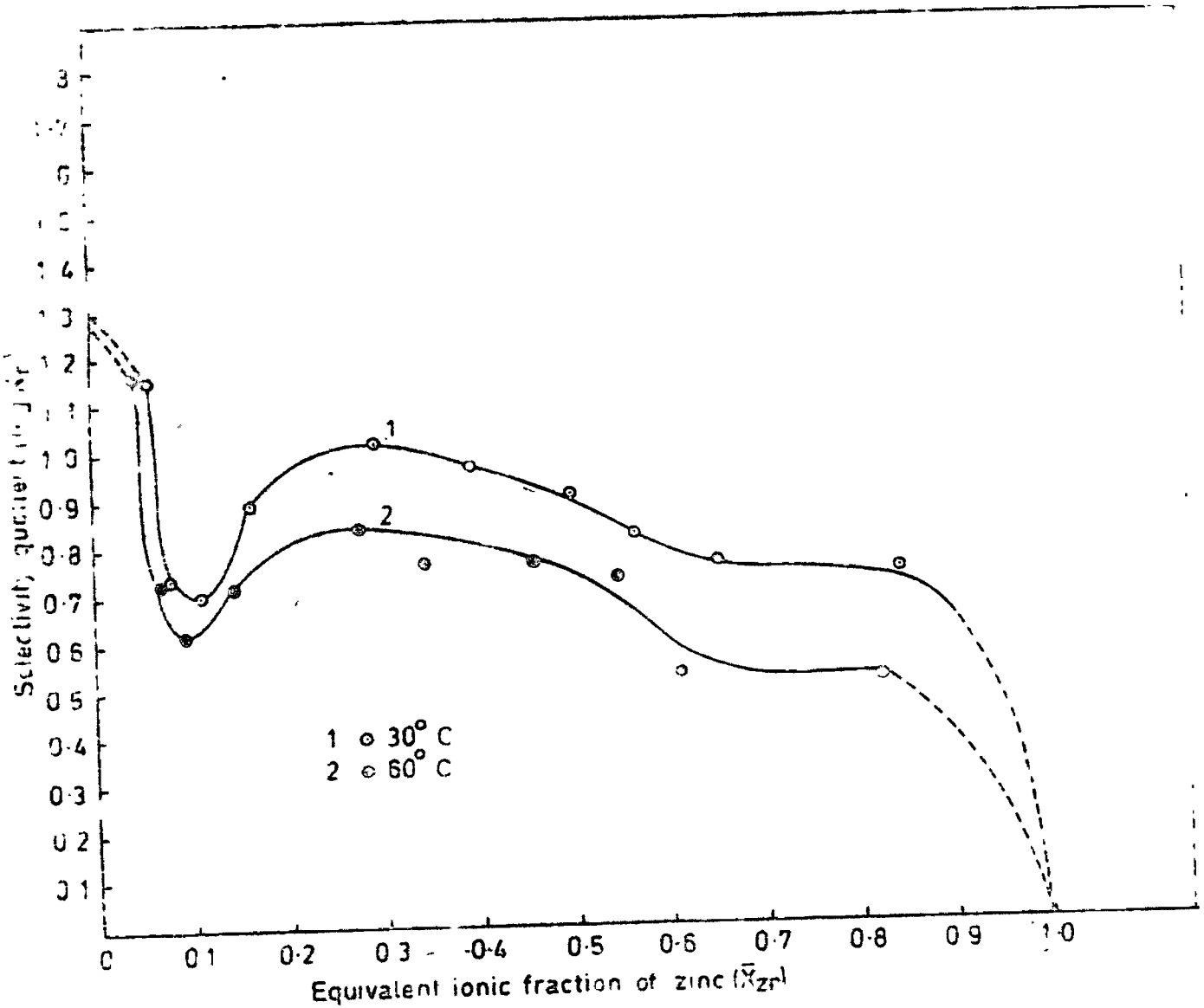


FIG 6 ZINC SODIUM SELECTIVITY IN MONTMORILLONITE

TABLE XXXI

Values of equivalent ionic fractions of zinc and sodium and selectivity quotients at 30°C for the zinc exchange with sodium montmorillonite

$\bar{X}_{Zn}$	X_{Zn}	$\bar{X}_{Na}$	X_{Na}	K_C	log K_C
0.058	0.004	0.942	0.996	14.1	1.15
0.075	0.014	0.925	0.986	5.4	0.73
0.107	0.023	0.893	0.977	5.0	0.70
0.166	0.026	0.834	0.974	7.8	0.89
0.299	0.048	0.701	0.952	10.6	1.02
0.395	0.091	0.605	0.909	9.2	0.97
0.499	0.164	0.501	0.836	8.2	0.91
0.562	0.250	0.438	0.750	6.6	0.82
0.650	0.366	0.350	0.633	6.0	0.77
0.843	0.677	0.157	0.322	5.6	0.75

TABLE XXXII

Values of equivalent ionic fractions of zinc and sodium and selectivity quotients at 60°C for the zinc exchange with sodium montmorillonite

$\bar{X}_{Zn}$	X_{Zn}	$\bar{X}_{Na}$	X_{Na}	K_C	log K_C
0.060	0.004	0.940	0.996	14.7	1.17
0.074	0.014	0.926	0.986	5.2	0.72
0.094	0.024	0.906	0.976	4.1	0.61
0.141	0.031	0.859	0.969	5.2	0.72
0.275	0.062	0.725	0.938	6.9	0.84
0.349	0.106	0.651	0.894	5.9	0.77
0.462	0.180	0.538	0.820	5.8	0.76
0.545	0.266	0.455	0.734	5.4	0.73
0.603	0.409	0.397	0.591	3.4	0.53
0.824	0.711	0.175	0.288	3.3	0.52

from the areas under the curves (Fig.16) using the trapezoidal rule. The values are given in table XXXIII. A higher value of K at 30° than at 60°C indicated a higher preference of zinc for the clay at the lower temperature. Further zinc was preferred over sodium by montmorillonite.

The standard free energy of exchange, ΔG° was calculated from the equation:

$$\Delta G^\circ = - RT \ln K \qquad \ldots\ldots\ldots\ldots (5)$$

and the standard enthalpy change ΔH° from van't Hoff isochore

$$\ln \left(\frac{K_{T_2}}{K_{T_1}} \right) = \frac{- \Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \qquad \ldots\ldots\ldots (6)$$

The standard entropy change, ΔS° was then obtained by the equation:

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \qquad \ldots\ldots\ldots (7)$$

The values are listed in table XXXIII.

During the exchange of sodium with zinc over montmorillonite the free energy change was negative over both the temperatures, that at 30°C being still more negative than the one at 60°C. At both the temperatures the exchanges were, therefore, spontaneous, the order of preference being zinc>sodium. The order of preference varied with temperature, being higher at 30° than 60°C. The results were in accordance with the earlier inferences.

Negative enthalpy change (Table XXXIII) indicated that the

TABLE XXXIII

Thermodynamic values of the zinc exchange on sodium montmorillonite at 30° and 60°C

Thermodynamic parameters	30°C	60°C
K	18.0	11.9
ΔG° (cal/mole)	-1742	-1628
ΔH° (cal/mole)	-2744	
ΔS° (cal/mole)	-3.3	-3.3

reaction was exothermic, or in other words the binding energy of 1 atom of zinc was lower than that of 2 atoms of sodium. Thus zinc was more tightly bound to montmorillonite than sodium. This was in accordance with the values of K_c being higher than unity (Tables XXXI and XXXII). The exchange was also ruled by entropy effects. The entropy loss was indicative of a greater order produced in the forward reaction during zinc transfer to montmorillonite. Entropy change included two reactions which occurred in the interface and the solution. In going from solution to solid phase some of the water of hydration of zinc ions was removed to give a more orderly structure of zinc ions on the surface with resultant immobilisation and reduction in the degrees of freedom of zinc ions on the clay surface. This contributed towards entropy loss. Further the passage of sodium ions from solid to water resulted in their enhanced hydration with greater ordering of water and a further entropy loss. Their is evidence to support these facts[8,9].

The surface phase activity coefficients of sodium and zinc ions were calculated from the following expressions[10];

$$\ln f_{Na} = \bar{X}_{Zn} \ln K_c - \int_0^{\bar{X}_{Zn}} \ln K_c \, d\bar{X}_{Zn} \qquad \ldots\ldots\ldots (8)$$

$$\text{and} \quad \ln f_{Zn} = \left(\bar{X}_{Zn} - 1\right) \ln K_c - \int_{X_{Zn}}^{1} \ln K_c \, d\bar{X} \qquad \ldots\ldots (9)$$

The values are given in tables XXXIV and XXXV. The values were indicative of a nonideal system resulting in an increase in heterogeneity in the distribution of sodium ions and a decrease in

TABLE XXXIV

The surface phase activity coefficients, excess free energies, enthalpies and entropies of mixing ΔG_m^x, ΔH_m^x, ΔS_m^x for sodium-zinc exchange with montmorillonite at 30°C

$\bar{x}_{Zn}$	f_{Na}	f_{Zn}	ΔG_m^x	ΔH_m^x	ΔS_m^x
0.058	1.01	0.01	-53.7	-222	-0.56
0.075	0.95	0.04	-177.1	-330	-0.51
0.107	0.94	0.05	-230.8	-402	-0.57
0.166	0.99	0.04	-325.7	-511	-1.61
0.299	1.06	0.06	-497.1	-937	-1.45
0.395	1.12	0.09	-545.2	-710	-0.55
0.499	1.07	0.14	-564.9	-882	-1.05
0.562	0.98	0.20	-556.3	-1117	-1.85
0.650	0.82	0.31	-504.3	-805	-0.99
0.843	0.89	0.54	-321.1	-959	-2.11

TABLE XXXV

The surface phase activity coefficients, excess free energies, enthalpies and entropies of mixing ΔG_m^x, ΔH_m^x, ΔS_m^x for sodium-zinc exchange with montmorillonite at 60°C

$\bar{x}_{Zn}$	f_{Na}	f_{Zn}	ΔG_m^x	ΔH_m^x	ΔS_m^x
0.060	1.03	0.02	-136.3	-274	-0.41
0.074	0.97	0.06	-156.8	-396	-0.72
0.094	0.95	0.08	-188.1	-437	-0.75
0.141	0.98	0.07	-258.3	-500	-0.73
0.275	1.08	0.09	-405.0	-1052	-1.94
0.349	1.03	0.13	-458.9	-680	-0.66
0.462	1.01	0.20	-489.9	-905	-1.25
0.545	0.96	0.28	-475.8	-1304	-2.48
0.603	0.75	0.39	-448.3	- 854	-1.22
0.824	0.74	0.68	-246.7	-1102	-2.52

heterogeneity in case of zinc ions on the solid surface. The results found support from the work of Deist and Talibudeen[11] on ion exchange in soils.

To further examine the deviation of the heterogeneous system from ideality, the excess thermodynamic functions for the system were calculated from the following expressions[12,8];

$$\Delta G_m^x = RT \left(\bar{X}_{Zn} \ln f_{Zn} + \bar{X}_{Na} \ln f_{Na} \right) \quad \ldots\ldots\ldots (10)$$

$$\Delta H_m^x = -RT^2 \; X_{Zn} \left[\left(\frac{\delta \ln f_{Zn}}{\delta T} \right) + X_{Na} \left(\frac{\delta \ln f_{Na}}{\delta T} \right) \right] \quad \ldots (11)$$

and $$\Delta G_m^x = \Delta H_m^x - T \Delta S_m^x \quad \ldots\ldots\ldots\ldots (12)$$

The values are given in tables XXXIV and XXXV. The values of ΔG_m^x were negative at both the temperatures which meant that with respect to the pure forms the heterogeneous surface phases were more stable than they would be if the mixing were ideal i.e., the deviation from ideality occurred in the sense of a more stable mixture. Negative enthalpies of mixing pointed to a more tightly bound mixture of sodium and zinc ions. The negative entropies of mixing were a pointer to a nonideal state of the mixture and a significant heterogeneity at the surface. The difference in the hydration rates of the ions in the mixture resulted in a decrease in entropy with respect to the homoionic forms.

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C H A P T E R - III

STUDIES ON THE KINETICS OF ZINC EXCHANGE ON Na-DICKITE

CHAPTER III

STUDIES ON THE KINETICS OF ZINC EXCHANGE ON Na-DICKITE

I N T R O D U C T I O N

The ion exchange reaction in clays and soils has proved of fundamental importance in agriculture and technology. Since the reaction involves transport of ions it is heterogeneous and cannot be dealt with by simple kinetic rate laws. Quite a bit of basic research has been reported on the kinetics of exchange reactions. Most of the investigations are based upon the pioneering work of Boyd et al.[1] on organic zeolities. Subsequent research has dealt with synthetic ion exchangers[2,3,4]. Information in regard to kinetics of exchange on soils and clays is meagre[5]. Several compounds of zinc find important applications as pesticides in modern agricultural production. Their degradation often gives rise to zinc residues. Zinc is an important trace metal and can correct micronutrient deficiency in soils in addition to pesticidal action of its parent compounds.

It was, therefore, considered relevant to investigate kinetics of zinc exchange on homoionic clays. To begin with clay mineral dickite, which is a polymorph of $Al_4(Si_4O_{10})(OH)_8$ was selected for this fundamental study.

E X P E R I M E N T A L

The dickite clay used in these studies was an American sample

collected from Mexico as already described. Its clay fraction was purified by sedimentation and centrifugation with an average particle size of 0.002 mm ($r \simeq 10^{-4}$cm).

PREPARATION OF SODIUM SATURATED DICKITE

Sodium saturated dickite was prepared from the above dickite as described earlier in Chapter I, Part I of this thesis.

DETERMINATION OF CONCENTRATION OF DICKITE SUSPENSION

The concentration of sodium dickite suspension was determined by evoporation as already described. The concentration of sodium dickite suspension was 18.0 g per litre.

CATION EXCHANGE CAPACITY

The base exchange capacity of the dickite was determined by Gangule's method as described earlier in Chapter I, Part II of this thesis. Its value was found to be 0.145 meq per g of Na-dickite.

ZINC EXCHANGE ON Na-DICKITE

The exchange reaction between Na-dickite and Zn^{++} could be represented as:

$$Na_x - \text{dickite} + y\ Zn^{++} \rightleftharpoons Zn_y - \text{dickite} + x\ Na^{+}$$

It could be either particle or film or mixed particle diffusion controlled reaction. The rate determining step of the above exchange was determined by (i) the interruption test[6], and (ii) by equation test[7].

✝ The interruption test[1] is the best experimental test for distinguishing particle and particle film control diffusion. During a kinetic experiment the exchanger beads are removed and quickly separated from adhering solution. After a brief period they are re-immersed in their solution and the experiment continued. If the control is due to particle diffusion, the rate immediately on re-immersion is enhanced. On the other hand, if the control is due to film diffusion, no concentration gradient exists in the exchanger and the interruption has no effect.

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INTERRUPTION TEST

The interruption test was carried out at 25°, 55° and 70°C at several dilutions of $Zn(NO_3)_2$ by withdrawal of $Zn(NO_3)_2$ solution from Na-dickite particles for a brief interval of time (5 minutes) and then adding the solution again. This was done at two time intervals viz. 10 minutes at 25°C and 30 minutes at 25°, 55° and 70°C. The concentration of Zn^{++} was estimated at different time intervals before and after the interruption. The results for two dilutions viz. 0.1N and 0.02N at two different time intervals are given in Fig.17 and tables XXXVI to XXXIX.

EQUATION TEST

The result obtained by the interruption test were confirmed by kinetic studies involving equation test. For this purpose a number of 10 ml samples of Na-dickite were taken in glass stoppered tubes, brought to the desired temperature, treated with fixed amounts of standard $Zn(NO_3)_2$ solution (0.1N and 0.02N) and the mixture adjusted to 25 ml with distilled water. The solutions were kept in contact for appropriate intervals of time without shaking. The contents were filtered and the concentration change in the suspensions determined using EDTA titration in case of Zn^{++} and flame photometry in case of Na^{+}. The corresponding concentration of sodium in the clay phase was obtained by substraction of sodium concentration in the equilibrium suspension from Na-CEC. Similarly the amount of zinc taken up by the clay surface in replacing sodium was obtained by difference between the amount of zinc added and the amount of zinc left behind in equilibrium suspension. This gave the

uptake of Zn^{++} as a function of time. The results are recorded in tables XL to XLIII.

The values of the fractional attainment of equilibrium were calculated from the relationship:

$$F = \frac{\text{amount of zinc adsorbed at time t}}{\text{maximum amount of zinc adsorbed}}$$

$$= \frac{C_o - C_t}{C_o - C_\infty}$$ where C_o = initial concentration of zinc, C_t = concentration of zinc at time t , C_∞ = concentration of zinc at equilibrium. The results at 25°, 40°, 55° and 70°C are recorded in tables XLIV to XLVII. The values of F were found to be the same at both the dilutions and hence further calculations were done at one dilution only (0.1N). A plot of the values of F against time is given in Fig.18, curves 1-4.

SEPARATION FACTOR

The separation factor was obtained from the equivalent concentrations of the zinc and sodium ions in the clay and solution phases. The equivalent ionic fractions of zinc and sodium in dickite ($\bar{X}_{Zn}$ and $\bar{X}_{Na}$) and in the solution (X_{Zn} and X_{Na}) were calculated from the expressions-

$$\bar{X}_{Zn} = \frac{\bar{C}_{Zn}}{\bar{C}}, \quad X_{Zn} = \frac{C_{Zn}}{C}$$

$$\bar{X}_{Na} = \frac{\bar{C}_{Na}}{\bar{C}} \text{ and } X_{Na} = \frac{C_{Na}}{C}$$, where $\bar{C}$ and C were the total concentrations of the ion concerned in the clay and solution

phases respectively. The results are given in tables XLVIII and XLIX.

FRACTIONAL PORE VOLUME

The pore volume of Na-dickite was calculated from the bulk and particle densities from the relationship:

$$\% \text{ pore space} = 100 - \frac{\text{Bulk density}}{\text{Particle density}} \times 100$$

For this purpose the bulk density of Na-dickite was determined with the help of R.D. bottle. The empty bottle was weighed without stopper and then weighed with clay filled up to the brim. The clay was then removed and replaced with water by means of a burette and noting the exact volume of water required to fill the bottle. The bulk density was obtained by dividing the weight of the clay with the volume of water.

The particle density was determined by taking an R.D. bottle filled with water and weighing it. Air dry 10 g clay was kept into a small beaker and few ml of water were added to it. This suspension was then boiled for a short time in order to expel all air. Water was then removed from the R.D. bottle and the clay suspension transferred to it and the bottle filled upto the brim with water. The weight of the clay divided by the weight of water displaced gave the particle density of dickite. Percentage pore space was then calculated. From the percentage pore space the fractional pore volume was calculated by dividing the pore space with 100. The results are recorded in table L.

TABLE XXXVI

Interruption test for Zn^{++} exchange on Na-dickite at 25°C

1. Concentration of clay suspension = 18.0 g per litre
2. Volume of clay suspension = 10.0 ml
3. Volume of zinc nitrate = 1.5 ml
4. Concentration of zinc nitrate solution = 0.1N and 0.02N
5. Total volume of mixture (Clay suspension + zinc nitrate + water) = 25.0 ml
6. Time of interruption = 10 min

Time in min	0.1N zinc nitrate solution			0.02N zinc nitrate solution		
	Volume of zinc in equilibrium suspension in ml	Meq of zinc adsorbed per 100 g clay	Fractional attainment of equilibrium (F)	Volume of zinc solution in equilibrium suspension in ml	Meq of zinc adsorbed per 100 g clay	Fractional attainment of equilibrium (F)
2	1.50	0.00	0.00	1.50	0.00	0.00
5	1.40	5.55	0.19	1.40	1.11	0.20
10	1.20	16.65	0.56	1.25	2.78	0.50
Interruption	- - -

TABLE XXXVII

Interruption test for Zn^{++} exchange on Na-dickite at 25°C

1. Concentration of clay suspension = 18.0 g per litre
2. Volume of clay suspension taken = 10.0 ml
3. Volume of zinc nitrate solution = 1.5 ml
4. Concentration of zinc nitrate solution = 0.1N and 0.02N
5. Total volume of mixture (Clay suspension + zinc nitrate + water) = 25.0 ml
6. Time of interruption = 30 min

Time in min	0.1N zinc nitrate solution			0.02N zinc nitrate solution		
	Volume of zinc in equilibrium suspension in ml	Meq of zinc adsorbed per 100 g clay	Fractional attainment of equilibrium (F)	Volume of zinc solution in equilibrium suspension in ml	Meq of zinc adsorbed per 100 g clay	Fractional attainment of equilibrium (F)
2	1.50	0.00	0.00	1.50	0.00	0.00
5	1.40	5.55	0.13	1.40	1.11	0.15
10	1.10	22.20	0.53	1.05	4.99	0.69
15	0.90	33.30	0.80	1.00	5.55	0.77
20	0.80	38.90	0.94	0.90	6.66	0.92
25	0.75	41.60	1.00	0.85	7.22	1.00
30	0.75	41.60	1.00	0.85	7.22	1.00
Interruption						
35	0.75	41.60	1.00	0.85	7.22	1.00
40	0.75	41.60	1.00	0.85	7.22	1.00
45	0.75	41.60	1.00	0.85	7.22	1.00
50	0.75	41.60	1.00	0.85	7.22	1.00
55	0.75	41.60	1.00	0.85	7.22	1.00

TABLE XXXVIII

Interruption test for Zn^{++} exchange on Na-dickite at 55°C

1. Concentration of clay suspension = 18.0 g per litre
2. Volume of clay suspension taken = 10.0 ml
3. Volume of zinc nitrate solution = 1.5 ml
4. Concentration of zinc nitrate solution = 0.1N and 0.02N
5. Total volume of mixture (Clay suspension + zinc nitrate + water) = 25.0 ml
6. Time of interruption = 30 min

Time in min	0.1N zinc nitrate solution			0.02N zinc nitrate solution		
	Volume of zinc in equilibrium suspension in ml	Meq of zinc adsorbed per 100 g clay	Fractional attainment of equilibrium (F)	Volume of zinc solution in equilibrium suspension in ml	Meq of zinc adsorbed per 100 g clay	Fractional attainment of equilibrium (F)
2	1.50	0.00	0.00	1.50	0.00	0.00
5	1.40	5.55	0.17	1.40	1.11	0.20
10	1.20	16.65	0.50	1.20	3.33	0.60
15	1.10	22.20	0.66	1.10	4.44	0.80
20	1.00	27.75	0.83	1.00	5.55	1.00
25	0.90	33.30	1.00	1.00	5.55	1.00
30	0.90	33.30	1.00	1.00	5.55	1.00
Interruption						
35	0.90	33.30	1.00	1.00	5.55	1.00
40	0.90	33.30	1.00	1.00	5.55	1.00
45	0.90	33.30	1.00	1.00	5.55	1.00
50	0.90	33.30	1.00	1.00	5.55	1.00
55	0.90	33.30	1.00	1.00	5.55	1.00

TABLE XXX

Interruption test for Zn^{++} exchange on Na-dickite at 70°C

1. Concentration of clay suspension = 18.0 g per litre
2. Volume of clay suspension taken = 10.0 ml
3. Volume of zinc nitrate solution = 1.5 ml
4. Concentration of zinc nitrate solution = 0.1N and 0.02N
5. Total volume of mixture (Clay suspension + zinc nitrate + water) = 25.0 ml
6. Time of interruption = 30 min

Time in min	0.1N zinc nitrate solution			0.02N zinc nitrate solution		
	Volume of zinc in equilibrium suspension in ml	Meq of zinc adsorbed per 100 g clay	Fractional attainment of equilibrium (F)	Volume of zinc solution in equilibrium suspension in ml	Meq of zinc adsorbed per 100 g clay	Fractional attainment of equilibrium (F)
2	1.50	0.00	0.00	1.50	0.00	0.00
5	1.40	5.55	0.20	1.40	1.11	0.25
10	1.35	13.88	0.50	1.30	2.22	0.50
15	1.15	19.43	0.70	1.20	3.33	0.75
20	1.00	27.75	1.00	1.10	4.44	1.00
25	1.00	27.75	1.00	1.10	4.44	1.00
30	1.00	27.75	1.00	1.10	4.44	1.00
Interruption	- - -

TABLE XL

Adsorption of zinc during kinetic study of zinc exchange on Na-dickite at different times, temperatures and at a dilution of 0.1N

Concentration of Na-dickite suspension = 18.0 g per litre

Volume of Na-dickite suspension = 10.0 ml

Volume of zinc nitrate = 1.5 ml

Total volume of mixture (Volume of clay suspension + zinc nitrate + water) = 25.0 ml

Temperature	Time in min	Volume of 0.1N EDTA solution used in titration	Volume of zinc adsorbed in ml	Meq. of zinc adsorbed per 100 g clay	Meq. of sodium in equilibrium suspension per litre	Meq. of sodium adsorbed per 100 g clay
25°C	0	0.00	0.00	0.00	0.00	0.00
	2	1.45	0.05	2.77	0.48	7.87
	5	1.40	0.10	5.55	0.44	8.47
	10	1.30	0.20	11.10	0.43	8.59
	15	1.20	0.30	16.65	0.39	9.08
	20	1.10	0.40	22.20	0.39	9.08
	25	1.00	0.50	27.75	0.37	9.44
	30	1.00	0.50	27.75	0.33	9.92
40°C	0	0.00	0.00	0.00	0.00	0.00
	2	1.45	0.05	2.78	0.49	7.74
	5	1.40	0.10	5.55	0.46	8.11
	10	1.30	0.20	11.10	0.44	8.47
	15	1.20	0.30	16.65	0.39	9.08
	20	1.10	0.40	22.20	0.37	9.56
	25	1.05	0.45	24.98	0.35	9.68
	30	1.05	0.45	24.98	0.35	9.68

TABLE XLI

Adsorption of zinc during kinetic study of zinc exchange on Na-dickite at different times, temperatures and at a dilution of 0.1N

Concentration of Na-dickite suspension = 18.0 g per litre

Volume of Na-dickite suspension = 10.0 ml

Volume of zinc nitrate = 1.5 ml

Total volume of mixture (Volume of clay suspension + zinc nitrate + water) = 25.0 ml

Temperature	Time in min	Volume of 0.1N EDTA solution used in titration	Volume of zinc adsorbed in ml	Meq. of zinc adsorbed per 100 g clay	Meq. of sodium in equilibrium suspension per litre	Meq. of sodium adsorbed per 100 g clay
	0	0.00	0.00	0.00	0.00	0.00
	2	1.45	0.05	2.77	0.53	7.14
	5	1.40	0.10	5.55	0.52	7.26
55°C	10	1.30	0.20	11.10	0.48	7.87
	15	1.20	0.30	16.65	0.44	8.35
	20	1.14	0.36	19.98	0.42	8.71
	25	1.10	0.40	22.20	0.37	9.44
	30	1.10	0.40	22.20	0.35	9.68
	0	0.00	0.00	0.00	0.00	0.00
	2	1.45	0.05	2.77	0.57	6.66
	5	1.40	0.10	5.55	0.53	7.14
70°C	10	1.30	0.20	11.10	0.52	7.26
	15	1.20	0.30	16.65	0.47	7.99
	20	1.18	0.32	17.76	0.45	8.23
	25	1.15	0.35	19.43	0.44	8.35
	30	1.15	0.35	19.43	0.39	9.08

TABLE XLII

Adsorption of zinc during kinetic study of zinc exchange on Na-dickite at different times, temperatures and at a dilution of 0.02N

Concentration of Na-dickite suspension = 18.0 g per litre

Volume of Na-dickite suspension = 10.0 ml

Volume of zinc nitrate = 1.5 ml

Total volume of mixture (Volume of clay suspension + zinc nitrate + water) = 25.0 ml

Temperature	Time in min	Volume of 0.1N EDTA solution used in titration	Volume of zinc adsorbed in ml	Meq. of zinc adsorbed per 100 g clay	Meq. of sodium in equilibrium suspension per litre	Meq. of sodium adsorbed per 100 g clay
25°C	0	0.00	0.00	0.00	0.00	0.00
	2	1.50	0.00	0.00	0.57	6.50
	5	1.40	0.10	1.11	0.57	6.50
	10	1.30	0.20	2.22	0.58	6.40
	15	1.20	0.30	3.33	0.60	6.20
	20	1.10	0.40	4.44	0.63	5.80
	25	1.00	0.50	5.55	0.68	5.10
	30	1.00	0.50	5.55	0.68	5.10
40°C	0	0.00	0.00	0.00	0.00	0.00
	2	1.50	0.00	0.00	0.57	6.50
	5	1.40	0.10	1.11	0.57	6.50
	10	1.30	0.20	2.22	0.57	6.50
	15	1.20	0.30	3.33	0.57	6.50
	20	1.10	0.40	4.44	0.59	6.30
	25	1.05	0.45	4.99	0.62	6.17
	30	1.05	0.45	4.99	0.65	6.45

TABLE XLIII

Adsorption of zinc during kinetic study of zinc exchange on Na-dickite at different times, temperatures and at a dilution of 0.02N

Concentration of Na-dickite suspension = 18.0 g per litre

Volume of Na-dickite suspension = 10.0 ml

Volume of zinc nitrate = 1.5 ml

Total volume of mixture (Volume of clay suspension + zinc nitrate + water) = 25.0 ml

Temperature	Time in min	Volume of 0.1N EDTA solution used in titration	Volume of zinc adsorbed in ml	Meq. of zinc adsorbed per 100 g clay	Meq. of sodium in equilibrium suspension per litre	Meq. of sodium adsorbed per 100 g clay
	0	0.00	0.00	0.00	0.00	0.00
	2	1.50	0.00	0.00	0.57	6.65
	5	1.40	0.10	1.11	0.61	6.05
55°C	10	1.28	0.22	2.44	0.62	5.93
	15	1.20	0.30	3.33	0.65	5.45
	20	1.14	0.36	3.99	0.68	5.08
	25	1.10	0.40	4.44	0.68	5.08
	30	1.10	0.40	4.44	0.57	6.50
	0	0.00	0.00	0.00	0.00	0.00
	2	1.50	0.00	0.00	0.58	6.41
	5	1.40	0.10	1.11	0.61	6.05
70°C	10	1.30	0.20	2.22	0.65	5.45
	15	1.22	0.28	3.11	0.69	5.20
	20	1.20	0.30	3.33	0.70	4.84
	25	1.15	0.35	3.89	0.70	4.84
	30	1.15	0.35	3.89	0.70	4.84

TABLE XLIV

Values of fractional attainment of equilibrium F, Bt and B during the kinetic study of Zn^{++} exchange on Na-dickite at different times, temperatures and a dilution of 0.1N

Volume of clay suspension = 10.0 ml

Initial concentration of zinc added (C_o) = 83.25 meq/100 g

Total volume of mixture (Volume of clay suspension + zinc nitrate + water) = 25.0 ml

Temperature	Time in min	Meq. of zinc in equilibrium suspension (Ct)	Meq. of zinc adsorbed per 100 g clay $(C_o - C_t)$	Fractional attainment of equilibrium $\left(\frac{C_o - C_t}{C_o - C_\infty}\right)$	Bt (From Reichenberg table)	$B\left(\frac{Bt}{t}\right)$
25°C	2	80.48	2.77	0.10	0.009	0.0046
	5	77.70	5.55	0.20	0.039	0.0077
	10	72.15	11.10	0.40	0.177	0.0177
	15	66.60	16.65	0.60	0.479	0.0319
	20	61.05	22.20	0.80	1.120	0.0560
	25	55.50	27.75	1.00	-	-
	30	55.50	27.75	1.00	-	-
40°C	2	80.48	2.77	0.11	0.011	0.0056
	5	77.70	5.55	0.22	0.047	0.0095
	10	72.15	11.10	0.44	0.222	0.0222
	15	66.60	16.65	0.67	0.647	0.0431
	20	61.05	22.20	0.80	1.620	0.0810
	25	58.20	24.98	1.00	-	-
	30	58.27	24.98	1.00	-	-

TABLE XLV

Values of fractional attainment of equilibrium F, Bt and B during the kinetic study of Zn^{++} exchange on Na-dickite at different times, temperatures and a dilution of 0.1N

Volume of clay suspension = 10.0 ml

Initial concentration of zinc added (C_o) = 83.25 meq/100 g

Total volume of mixture (Volume of clay suspension + zinc nitrate + water) = 25.0 ml

Temperature	Time in min	Meq. of zinc in equilibrium suspension (C_t)	Meq. of zinc adsorbed per 100 g clay ($C_o - C_t$)	Fractional attainment of equilibrium $\left(\frac{C_o - C_t}{C_o - C_\infty}\right)$	Bt (From Reichenborg table)	$B\left(\frac{Bt}{t}\right)$
55°C	2	80.48	2.77	0.125	0.156	0.0078
	5	77.70	5.55	0.250	0.062	0.0125
	10	72.15	11.10	0.500	0.287	0.0287
	15	66.60	16.65	0.750	0.905	0.0603
	20	63.27	19.98	0.900	1.800	0.0900
	25	61.05	22.20	1.000	-	-
	30	61.05	22.20	1.000	-	-
70°C	2	80.48	2.77	0.143	0.018	0.0092
	5	77.70	5.55	0.286	0.086	0.0172
	10	72.15	11.10	0.571	0.419	0.0419
	15	66.60	16.65	0.800	1.120	0.0750
	20	65.49	17.76	0.910	1.190	0.0955
	25	63.82	19.43	1.000	-	-
	30	63.82	19.43	1.000	-	-

TABLE XLVI

Values of fractional attainment of equilibrium F, Bt and B during the kinetic study of Zn^{++} exchange on Na-dickite at different times, temperatures and a dilution of 0.02N

Volume of clay suspension = 10.0 ml

Initial concentration of zinc added (C_o) = 16.65 meq/100 g

Total volume of mixture (Volume of clay suspension + zinc nitrate + water) = 25.0 ml

Temperature	Time in min	Meq. of zinc in equilibrium suspension (C_t)	Meq. of zinc adsorbed per 100 g clay ($C_o - C_t$)	Fractional attainment of equilibrium $\left(\frac{C_o - C_t}{C_o - C_\infty}\right)$	Bt (From Reichenberg table)	$B\left(\frac{Bt}{t}\right)$
	2	16.65	0.00	0.00	-	-
	5	15.54	1.11	0.20	0.039	0.0099
	10	14.43	2.22	0.40	0.177	0.0177
25°C	15	13.32	3.33	0.60	0.479	0.0319
	20	12.21	4.44	0.80	1.120	0.0560
	25	11.10	5.55	1.00	-	-
	30	11.10	5.55	1.00	-	-
	2	16.65	0.00	0.00	-	-
	5	15.54	1.11	0.22	0.047	0.0095
	10	14.21	2.22	0.44	0.222	0.0222
40°C	15	13.32	3.33	0.67	0.647	0.0431
	20	12.21	4.44	0.89	1.710	0.0850
	25	11.66	4.99	1.00	-	-
	30	11.66	4.99	1.00	-	-

TABLE XLVII

Values of fractional attainment of equilibrium F, Bt and B during the kinetic study of Zn^{++} exchange on Na-dickite at different times, temperatures and a dilution of 0.02N

Volume of clay suspension = 10.0 ml

Initial concentration of zinc added (C_o) = 16.65 meq/100 g

Total volume of mixture (Volume of clay suspension + zinc nitrate + water) = 25.0 ml

Temperature	Time in min	Meq. of zinc in equilibrium suspension (C_t)	Meq. of zinc adsorbed per 100g clay ($C_o - C_t$)	Fractional attainment of equilibrium $\left(\frac{C_o - C_t}{C_o - C_\infty}\right)$	Bt (From Reichenberg table)	$B\left(\frac{Bt}{t}\right)$
	2	16.65	0.00	0.00	-	-
	5	15.54	1.11	0.25	0.062	0.0125
	10	14.21	2.44	0.55	0.382	0.0382
55°C	15	13.32	3.33	0.75	0.905	0.0603
	20	12.66	3.99	0.90	1.800	0.0900
	25	12.21	4.44	1.00	-	-
	30	12.21	4.44	1.00	-	-
	2	16.65	0.00	0.00	-	-
	5	15.54	1.11	0.29	0.086	0.0172
	10	14.43	2.22	0.57	0.419	0.0419
70°C	15	13.54	3.11	0.80	1.070	0.0713
	20	13.32	3.33	0.91	1.910	0.0955
	25	12.76	3.89	1.00	-	-
	30	12.76	3.89	1.00	-	-

TABLE XLVIII

Values of equivalent ionic fractions of zinc and sodium and the separation factors at 25° and 40°C during the kinetic study of Zn^{++} exchange on Na-dickite at different times and a dilution of 0.1N (calculated from values given in table XL)

Temperature	Time in min.	$\bar{X}_{Zn}$	X_{Zn}	$\bar{X}_{Na}$	X_{Na}	α^{Zn}_{Na}
	2	0.261	0.924	0.739	0.076	0.029
	5	0.396	0.929	0.604	0.071	0.059
	10	0.564	0.924	0.436	0.076	0.106
25°C	15	0.647	0.925	0.353	0.075	0.149
	20	0.710	0.919	0.290	0.081	0.216
	25	0.746	0.915	0.254	0.085	0.262
	30	0.736	0.924	0.264	0.076	0.229
	2	0.264	0.922	0.736	0.078	0.033
	5	0.406	0.919	0.534	0.081	0.067
	10	0.567	0.922	0.433	0.078	0.111
40°C	15	0.647	0.925	0.353	0.075	0.149
	20	0.699	0.922	0.301	0.078	0.196
	25	0.721	0.923	0.279	0.077	0.216
	30	0.721	0.923	0.279	0.077	0.216

TABLE XLIX

Values of equivalent ionic fractions of zinc and sodium and the separation factors at 55° and 70°C during the kinetic study of Zn^{++} exchange on Na-dickite at different timesaand a dilution of 0.1N (calculated from values given in table XLI)

Temperature	Time in min.	$\bar{X}_{Zn}$	X_{Zn}	$\bar{X}_{Na}$	X_{Na}	α^{Zn}_{Na}
	2	0.269	0.916	0.731	0.084	0.034
	5	0.433	0.915	0.567	0.085	0.079
	10	0.585	0.915	0.515	0.085	0.106
55°C	15	0.666	0.916	0.334	0.084	0.184
	20	0.696	0.916	0.304	0.084	0.209
	25	0.702	0.934	0.298	0.066	0.166
	30	0.696	0.937	0.304	0.063	0.153
	2	0.294	0.911	0.706	0.089	0.041
	5	0.437	0.914	0.563	0.086	0.073
	10	0.377	0.912	0.263	0.088	0.138
70°C	15	0.676	0.920	0.324	0.080	0.181
	20	0.683	0.913	0.317	0.087	0.205
	25	0.699	0.913	0.301	0.087	0.221
	30	0.682	0.922	0.318	0.078	0.181

TABLE L

Determination of bulk density, particle density and fractional pore volume of Na-dickite

Bulk density			Particle density				Fractional pore volume	
Wt. of clay in g	Wt. of equal volume of water in g	Bulk density = Wt.of clay / Equal volume of water in g per cc	Wt. of water taken in g	Wt. of clay taken in g	Wt. of water displaced by clay in g	Particle density = Wt.of clay / Wt.of water displaced by clay in g per cc	% Pore space = 100 - Bulk density / Particle density x 100	Fractional pore volume
30.31	18.95	1.60	18.95	10.0	3.85	2.60	38.5	0.385

RESULTS AND DISCUSSION

According to Boyd et al.[1] the rate determining step in ion exchange processes is either an interdiffusion of ion in the exchanger particle or in the film. An examination of Fig.17 for the exchange of Zn on Na-dickite at 0.1N and 0.02N dilutions and several temperatures showed that the removal of $Zn(NO_3)_2$ solution from contact with Na-dickite and its reimmersion after a brief period or an interruption in the reaction did not cause a change in the rate of exchange. Thus, no concentration gradient was found to exist in the clay and the rate depended on the concentration difference across the film. Thus the rate determining step in the exchange of zinc with Na-dickite was governed by film diffusion at all the temperatures and dilutions of Zn^{++} ions studied.

The nature of the rate determining step was further confirmed by evaluating and finding out whether

$$\phi = \frac{\bar{C}\,\bar{D}\,S}{C\,D\,r_o}\,(5 + 2\,\alpha_{A/B}) \text{ was } \ll 1 \text{ or } \gg 1 \qquad \ldots\ldots(1)$$

In the above expression $\bar{C}$ was concentration of fixed ionic groups taken as equivalent to maximum adsorption (in view of negligible swelling in dickite) and C was total concentration of the counterion in solution in meq.cm^{-3}. The value of the radius of dickite particle, r_o, was taken as 10^{-4}cm, the film thickness, δ, was taken as 10^{-2}cm in unstirred solution and $\alpha_{A/B}$, the separation factor was calculated from equivalent ionic fractions as per the expression:

$$\alpha^{Zn^{++}}_{Na^{+}} = \bar{X}_{Zn} \cdot X_{Na} \Big/ \bar{X}_{Na} \cdot X_{Zn}$$

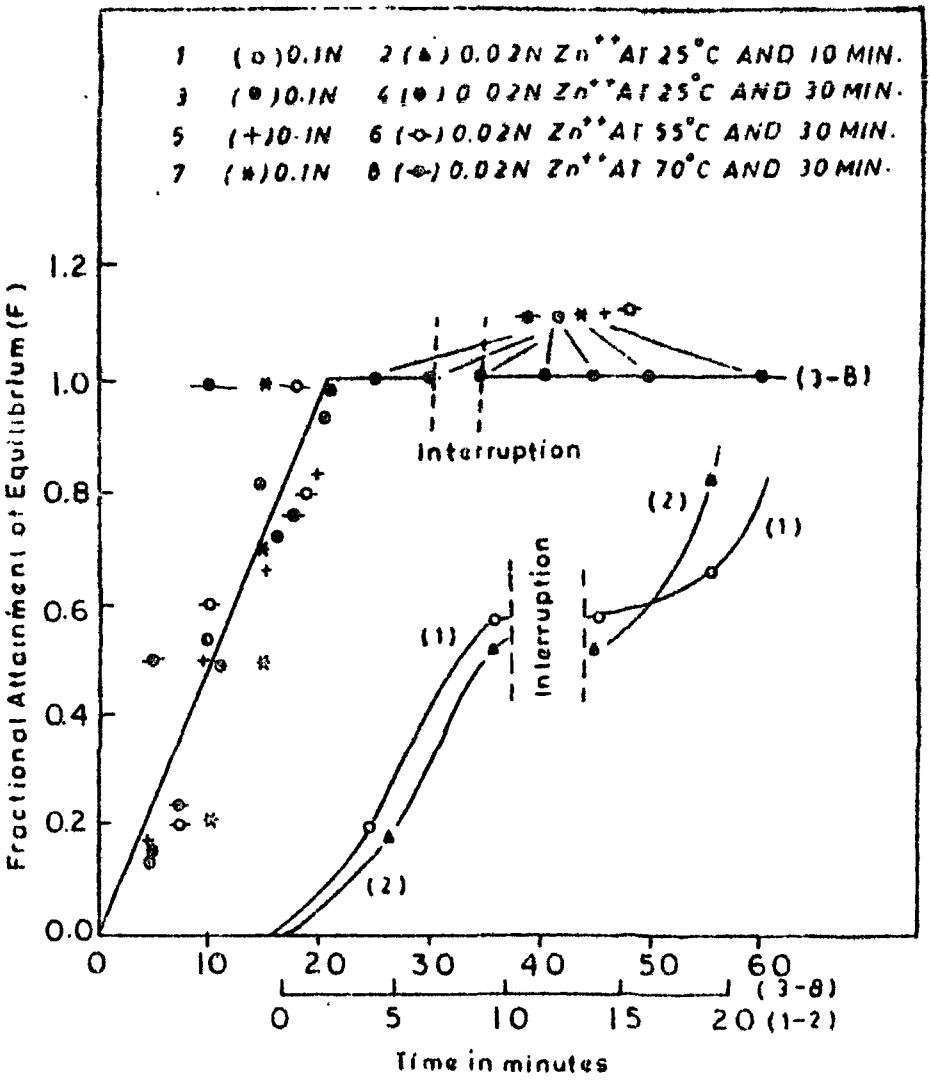

FIG 17 PLOT OF FRACTIONAL ATTAINMENT OF EQUILIBRIUM VS. TIME FOR ZINC EXCHANGE ON Na-DICKITE AT DIFFERENT CONCENTRATIONS TIMES AND TEMPERATURES

and as per results given in tables XLVIII and XLIX. The value of $\bar{D}$, the interdiffusion coefficient in the dickite phase was calculated from the relationship: $\bar{D} = \frac{Br_o^2}{\pi^2}$. The value of B was obtained from the plot Bt vs. t (Fig.19), the values of Bt having been obtained from suitable valuesof F as tabulated by Reichenberg[8]. The value of D, the aqueous phase diffusion coefficient in absence of the matrix which was taken as equal to diffusion in the film was obtained from Wheelers' relationship[9]: $\bar{D} = \frac{D\epsilon}{\delta}$, where ϵ was the pore volume of dickite. All the results are given in tables LI and LII.

Substitution of the above values in equation (1) and its evaluation gave values much greater than unity (tables LI and LII) confirming thereby that exchange rate was controlled by film diffusion at both the dilutions of Zn^{++} ions (0.1N and 0.02N). The solution concentration did not affect the rate controlling step.

The plot of F vs. t (Fig.18) showed that the exchange of Zn^{++} on Na-dickite was characterised by a rapid initial exchange followed by subsequent falling off in the rate as the concentration gradient diminished within the film. It was also clear from the plot that as the temperature increased from 25° to 70°C the rate of exchange increased. This was due to the fact that with increasing temperature the mobility of Zn^{++} ions increased. The half times of exchange at 0.1N and 0.02N derived from the equation

$$t_{\frac{1}{2}} = 0.23 \frac{r_o \delta \bar{C}}{DC} \qquad \ldots\ldots\ldots\ldots (2)$$

and also given in tables LIII to LVI. The $t_{\frac{1}{2}}$ decreased with an

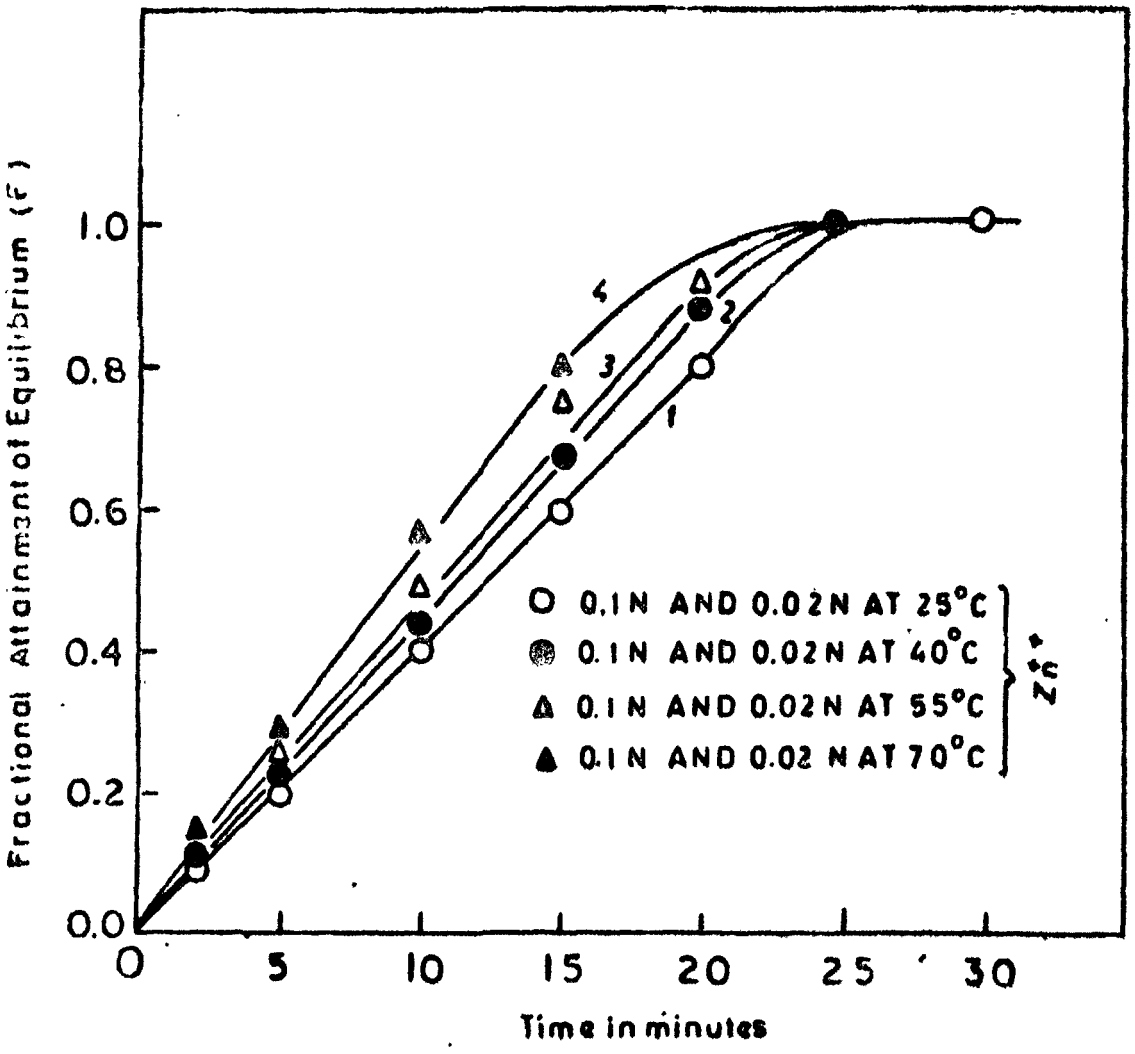

FIG. 18 PLOT OF FRACTIONAL ATTAINMENT OF EQUILIBRIUM VS. TIME FOR ZINC EXCHANGE ON SODIUM DICKITE AT DIFFERENT TEMPERATURES

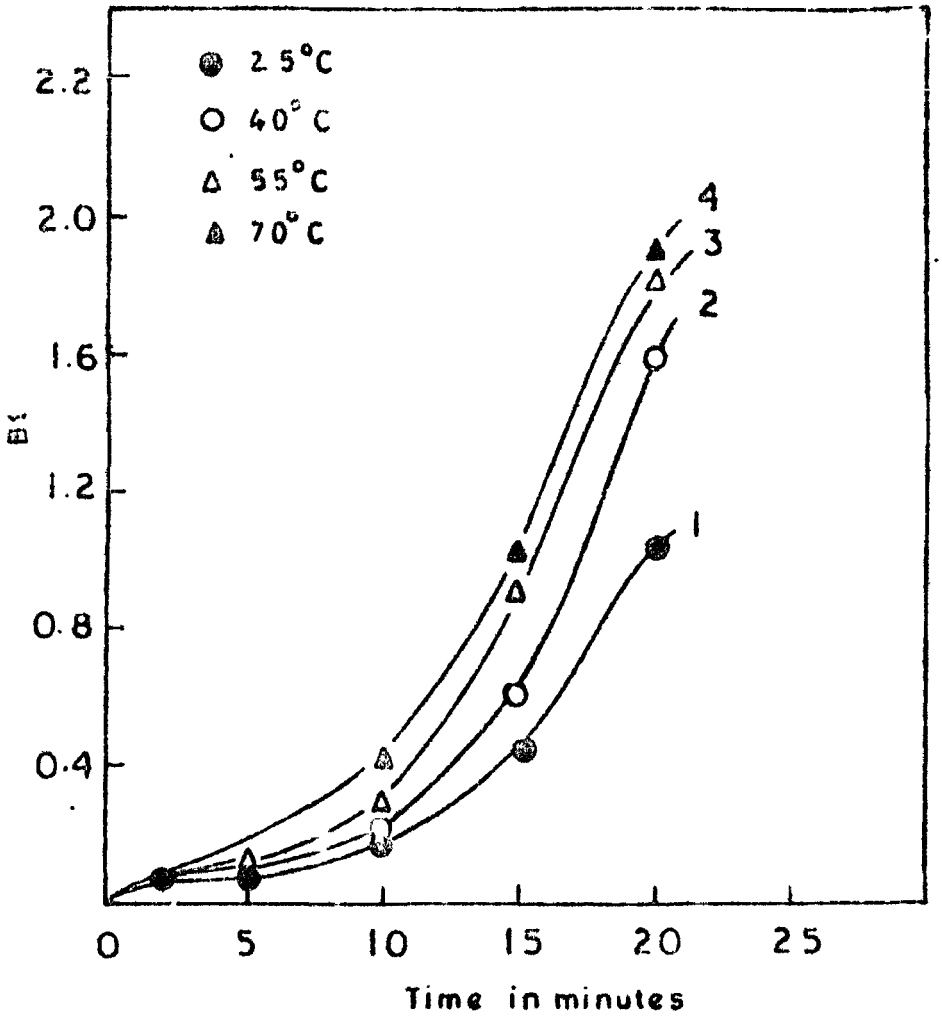

FIG. 19 PLOTS OF Bt VS. TIME FOR Zn^{++} EXCHANGE ON Na - DICKITE AT DIFFERENT TEMPERATURES

TABLE LI

Diffusion coefficients and ϕ values during the kinetic study of Zn^{++} exchange on Na-dickite at different times, temperatures and a dilution of 0.1N

Temperature	Time in min	Value of B	Interdiffusion coefficient in solid phase $\bar{D} = \frac{Br_o^2}{\pi^2}$	Aqueous phase diffusion coefficient $D = \frac{2\bar{D}}{\epsilon}$	$\phi = \frac{\bar{C}\bar{D}\delta}{C D r_o}(5+2\alpha A/B)$
25°C	2	0.0046	4.60×10^{-12}	2.40×10^{-11}	184
	5	0.0077	7.30×10^{-12}	3.70×10^{-11}	200
	10	0.0177	17.90×10^{-12}	9.30×10^{-11}	212
	15	0.0319	32.30×10^{-12}	16.80×10^{-11}	233
	20	0.0560	56.70×10^{-12}	29.50×10^{-11}	262
	25	-	-	-	-
	30	-	-	-	-
40°C	2	0.0056	5.60×10^{-12}	2.90×10^{-11}	168
	5	0.0095	9.60×10^{-12}	5.00×10^{-11}	176
	10	0.0222	22.50×10^{-12}	11.70×10^{-11}	193
	15	0.0431	43.60×10^{-12}	22.60×10^{-11}	213
	20	0.0810	82.00×10^{-12}	42.60×10^{-11}	236
	25	-	-	-	-
	30	-	-	-	-

TABLE LII

Diffusion coefficients and values during the kinetic study of Sn^{++} exchange on Na-dickite at different times, temperatures and a dilution of 0.1N

Temperature	Time in min	Value of B	Interdiffusion coefficient in solid phase $\bar{D} = \frac{Br_o^2}{\pi^2} \times 10^{-12}$	Aqueous phase diffusion coefficient $D = \frac{2\bar{D}}{\epsilon} \times 10^{-11}$	$\phi = \frac{\bar{C}\,\bar{D}\,\delta}{C\,D\,r_o}(5+2\alpha_{A/B})$
	2	0.0078	7.90	4.10	105
	5	0.0125	12.60	6.50	158
	10	0.0287	29.00	15.10	171
55°C	15	0.0603	61.00	31.70	191
	20	0.0900	91.10	47.30	209
	25	-	-	-	-
	30	-	-	-	-
	2	0.0092	9.30	4.80	104
	5	0.0172	17.40	9.00	137
	10	0.0419	42.40	22.00	150
70°C	15	0.0750	76.00	39.40	171
	20	0.0955	96.70	50.20	184
	25	-	-	-	-
	30	-	-	-	-

TABLE LXII

Half time ($t_{\frac{1}{2}}$) in hours during the kinetic study of Zn^{++} exchange on Na-dickite at different times, temperatures and a dilution of 0.1N

Temperature	Time in min	Concentration of fixed ionic group in meq cm^{-3} ($\bar{C}$)	Total concentration of the counterion in solution in meq cm^{-3} (C)	$t_{\frac{1}{2}} = 0.23 \frac{r_o \delta \bar{C}}{DC}$
25°C	2	0.275	0.145	30.4
	5	0.275	0.140	20.6
	10	0.275	0.130	8.6
	15	0.275	0.120	5.2
	20	0.275	0.110	3.3
40°C	2	0.250	0.145	22.8
	5	0.250	0.140	13.8
	10	0.250	0.130	6.3
	15	0.250	0.120	3.5
	20	0.250	0.110	2.0

TABLE LIV

Half time ($t_{\frac{1}{2}}$) in hours during the kinetic study of Zn^{++} exchange on Na-dickite at different times, temperatures and a dilution of 0.1N

Temperature	Time in min	Concentration of fixed ionic group in meq cm^{-3} ($\bar{C}$)	Total concentration of the counterion in solution in meq cm^{-3} (C)	$t_{\frac{1}{2}} = 0.23 \frac{r_o \delta \bar{C}}{DC}$
55°C	2	0.222	0.145	14.3
	5	0.222	0.140	9.5
	10	0.222	0.130	4.3
	15	0.222	0.120	2.2
	20	0.222	0.110	1.6
70°C	2	0.194	0.145	10.7
	5	0.194	0.140	5.9
	10	0.194	0.130	2.6
	15	0.194	0.120	1.7
	20	0.194	0.110	1.3

TABLE LV

Half time ($t_{\frac{1}{2}}$) in hours during the kinetic study of Zn^{++} exchange on Na-dickite at different times, temperatures and a dilution of 0.02N

Temperature	Time in min	Concentration of fixed ionic group in meq cm^{-3} ($\bar{C}$)	Total concentration of the counterion in solution in meq cm^{-3} (C)	$t_{\frac{1}{2}} = 0.23 \frac{r_o \delta \bar{C}}{DC}$
25°C	2	0.000	0.00	-
	5	0.055	0.14	41.2
	10	0.055	0.13	17.4
	15	0.055	0.12	10.5
	20	0.055	0.11	6.5
40°C	2	0.000	0.00	-
	5	0.050	0.14	27.5
	10	0.050	0.13	12.6
	15	0.050	0.12	7.1
	20	0.050	0.11	4.1

TABLE LVI

Half time ($t_{\frac{1}{2}}$) in hours during the kinetic study of Zn^{++} exchange on Na-dickite at different times, temperatures and a dilution of 0.02N

Temperature	Time in min	Concentration of fixed ionic group in meq cm^{-3} ($\bar{C}$)	Total concentration of the counterion in solution in meq cm^{-3} (C)	$t_{\frac{1}{2}} = 0.23 \frac{r_o \delta \bar{C}}{DC}$
55°C	2	0.000	0.000	-
	5	0.044	0.140	18.40
	10	0.044	0.128	8.70
	15	0.044	0.120	4.40
	20	0.044	0.114	3.10
70°C	2	0.000	0.000	-
	5	0.039	0.140	11.80
	10	0.039	0.130	5.20
	15	0.039	0.122	3.10
	20	0.039	0.118	2.50

increase in time of contact and with increasing amount of Zn^{++} ions added i.e. the rates of exchange as characterised by half times increased with time of contact and concentration of zinc. The later behaviour which has been noticed by other workers[5] also is characteristic of all ion exchange processes controlled by film diffusion. The $t_{\frac{1}{2}}$ values also decreased with a rise in temperature confirming *the earlier inference drawn from F vs. t plot on the rate of exchange* of Zn^{++} ions on Na-dickite.

An examination of tables LI and LII indicated that at both the concentrations of Zn^{++} ions and at all temperatures under study the rate of diffusion in the aqueous phase or film (D) was about 10 times faster than in the dickite phase ($\bar{D}$). The results also showed that the diffusion coefficients in both the phases increased with passage of time as well as with a rise in temperature, or in other words the rate of exchange of Zn^{++} ion on Na-dickite increased with time and a rise in temperature, a behaviour similar with the earlier inference on rate of exchange. The diffusion coefficients, however, were not affected by concentration of Zn^{++} ions in the concentration range studied by us.

Since temperature effect has proved very useful in providing an insight into the theory of all rate processes, the energetics of zinc exchange on Na-dickite were examined by temperature studies. The diffusion coefficient is related to temperature according to an Arrhenius type expression[10]

$$D = D_0 e^{-E_a/RT} \qquad \ldots\ldots\ldots\ldots (3)$$

From the values of D at several temperatures and the linear

relationship between log D and 1/T, D_o was calculated by extrapolation (Fig.20). This enabled the average energy of activation E_a to be calculated by expression (3) above. From this followed the enthalpy of activation

$$\Delta H_a = E_a - RT \qquad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

The entropy of activation ΔS_a was calculated from the relationship[11]

$$D_o = 2.72\, d\, \frac{kT}{h}\, e^{\Delta S_a/R} \qquad \ldots\ldots\ldots\ldots (5)$$

where d was the ionic jump distance (5×10^{-9}cm), k = the Boltzmann constant, h = the Planck constant, R = the gas constant and T, taken as 273°A. The free energy of activation ΔG_a was then determined from

$$\Delta G_a = \Delta H_a - T\, \Delta S_a \qquad \ldots\ldots\ldots\ldots (6)$$

The results for the kinetic parameters are given in table LVII.

An examination of table LVII showed an E_a range from 3.41 to 4.58 kcal $mole^{-1}$ for the exchange of Zn^{++} on Na-dickite. The energy of activation has proved useful in giving an idea of the nature of a reaction and values ranging from 2 to 5 kcal $mole^{-1}$ have been ascribed to exchange reactions controlled by film diffusion[12,13] without steric hindrance. The activation energies thus lent support to the deductions drawn above on the interaction of zinc with Na-dickite.

An examination of table LVII further showed that the enthalpy

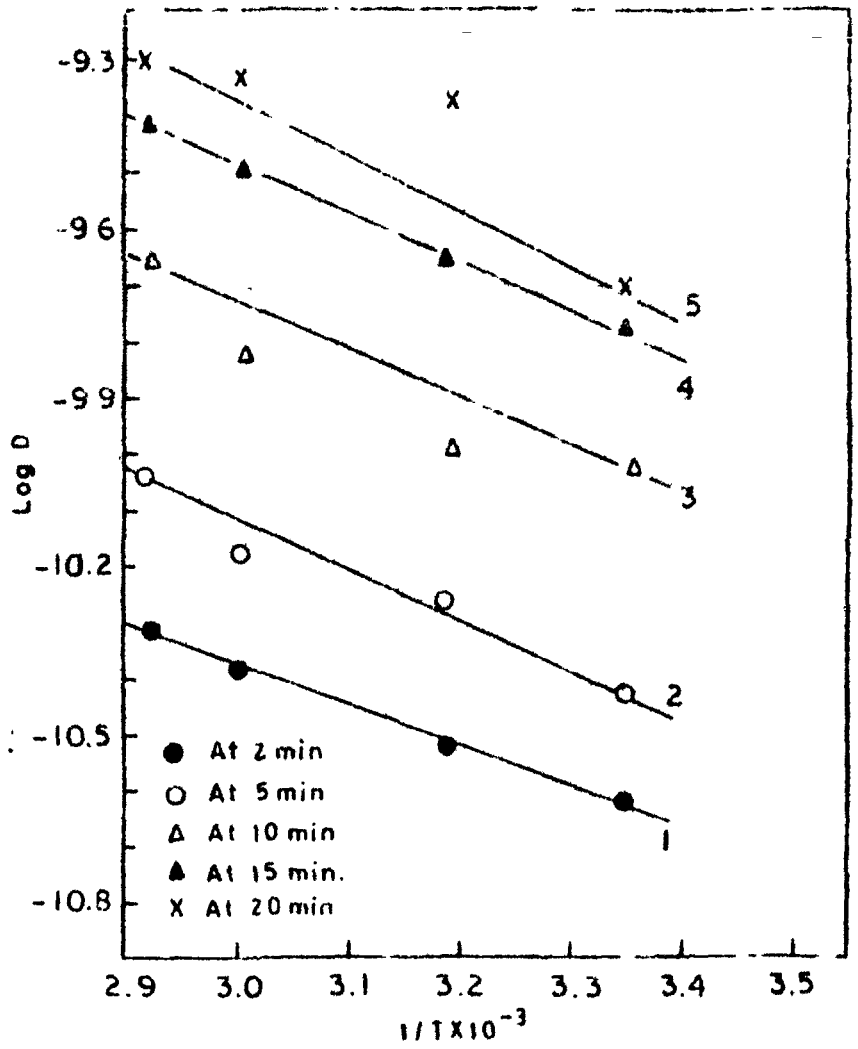

FIG. 20 PLOTS OF LOG D VS. $1/T \times 10^{-3}$ AT DIFFERENT TIME INTERVALS

TABLE LVII

Kinetic parameters for Zn^{++} exchange on Na-dickite at different temperatures and times

Temperature (°K)	Range of time (in min)	Range of E_a (kcal mole^{-1})	Range of ΔH_a (kcal mole^{-1})	Range of ΔS_a (cal degree^{-1} mole^{-1})	Range of ΔG_a (kcal mole^{-1})
298	2 to 20	3.41 to 4.58	2.82 to 3.99	-32.3 to -30.3	12.4 to 13.0
313	2 to 20	3.41 to 4.58	2.77 to 3.96	-32.3 to -30.4	12.9 to 13.4
328	2 to 20	3.41 to 4.58	2.75 to 3.93	-32.4 to -30.4	13.4 to 13.9
343	2 to 20	3.41 to 4.58	2.72 to 3.90	-32.4 to -30.4	13.8 to 14.3

of activation decreased with a rise in temperature or the rate of exchange of the Zn^{++} ions increased as the temperature of the reaction went up, an inference in accordance with the earlier conclusions. The reaction was also controlled by entropy of activation. From the standpoint of simple collision theory negative ΔS_a values (table LVII) pointed to a slow exchange of Zn^{++} ions over Na-dickite with formation of a more rigid activated structure with lesser randomness of motion for the Zn^{++} ions[14]. The free energy of activation ΔG_a (table LVII) for the exchange reaction had a tendency to increase with rise in temperature. Since the free energy of activation[14] influences the rate of a reaction, the rate of exchange of zinc over Na-dickite decreased with a rise in temperature, a fact which was in variance with the earlier inferences over the interaction.

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C H A P T E R - IV

STUDIES ON THE INFLUENCE OF A PESTICIDE (D-D MIXTURE) ON SOME NUTRIENT OF SOILS

CHAPTER IV

STUDIES ON THE INFLUENCE OF A PESTICIDE (D-D MIXTURE) ON SOME NUTRIENT OF SOILS

I N T R O D U C T I O N

Pesticides are widely used in agricultural production. They are used as insecticides, herbicides, fungicides and nematocides. Their use is attendent with varied physical, chemical and biological changes in soils[1,2]. They have an important influence on the microbial population and hence affect the nutrient status of the soil. During application they are partly adsorbed by the soil from where they may be released slowly again. They are responsible for important mineral transformations and solubilising effects. A lot of work on the major nutrient availability in soils in presence of pesticides has been reported by Freney[3], Castro[4], Wedding et al.[5], Alexander[6], Thiegs[7] as well as Shanker and Kumar[8]. Their findings were, however, not entirely in agreement.

Among pesticides, soil fumigants are widely used in present day agriculture to obtain high yield of crops. Carbon disulphide, ethylene dibromide, methyl bromide, nemagon and telone have been extensively tried for the control of nematodes, fungus and other microbial pests[9,10]. The interaction of the fumigants with soil ingredients have been useful as well as inhibitory[2] to plant nutrients. The cumulative effects of adsorption, persistance and degradation of the nematocides in soil may result in toxic[11] and

pollution hazards. While a considerable amount of work has been reported on the pesticidal and biological[12] properties of these chemicals, the role of the physical and chemical effects produced in soil by the above nematocides is, however, not properly understood.

In view of the importance of fumigation in crop production it was considered desirable to investigate the effect of a widely used nematocide (D-D mixture) on two soils of diverse nature and origin viz. a black cotton soil and a saline sodic soil as measured by any possible changes in the electrical conductivity, pH, organic matter, nitrogen, phosphorus and potassium content of the soil at different time intervals of fumigation. It was thought that this information will be of considerable interest in the efficient utilisation of the chemical in soils.

EXPERIMENTAL

Two soils of diverse origin and nature which occur widely in India and other parts of the world were selected for this study. They were a black cotton soil and a sodic saline soil. The black cotton soil used in the study (depth 0-30 cm) was collected from a representative area (Benkhera town) in Kota district (Rajasthan, India). For the collection of the soil sample a number of suitable spots were marked in a cultivated area and surface samples collected with the help of wooden and iron implements. The samples were then all mixed uniformly to form a representative sample of the area. The soil was then packed in plastic bags to avoid external contamination. It was then dried, crushed and sieved through a 4 mm

sieve. This soil belonged to the vertisol order and Mazustert great group. It was formed by weathering of basaltic rocks, was a dark grey montmorillonitic clay loam with crumb structure and a clayey texture.

The other soil was collected from the barren fields around Aligarh Muslim University in tehsil Koil of Aligarh district in Uttar Pradesh. This soil known as type III occurs widely in the central low lying tracks of the district. Surface samples from a depth of 0-30 cm were collected from a number of spots and then uniformly mixed to form a representative sample of the area. The colour of the soil varied from yellowish to grey, with loamy texture and a puddled structure. The area showed salt efflorescence and the soil effervesced with dilute HCl. The soil belonged to the aridosol order, central lowland series and was sodic saline in nature. The physico-chemical characteristics of both the soils were determined and are given in table LVIII A+B

The organic chemical used as a pesticide for nematocidal action in the soil was a mixture of 1,3-dichloropropene $\begin{matrix} Cl \\ H \end{matrix} > C = CH - CH_2 - Cl$ and 1,2-dichloropropane $Cl - CH_2 - \overset{H}{\underset{Cl}{C}} - CH_3$ in 50:50 ratio along with a few minor impurities. The combination commercially known as D-D mixture is extensively used for the control of nematode and fungus diseases in soils.

The soil fumigation experiments were conducted in thirty six earthenware pots of 25 x 25 cm size. The pots were cleaned and

coated with coaltar to prevent adsorption of water.

Samples weighing two kilograms each of the soils were taken in each of the thirty six pots. Zero day samples were drawn from the pots. The soil samples were then saturated with 25% distilled water by weight. Six doses of D-D mixture (0.00, 0.25, 0.50, 0.75, 1.00 and 1.25 ml per kg) were injected at a depth of 15 cm in three replications without growing any crop in the pots. All the samples were watered with 150 ml distilled water per week throughout the period of experiments. Distilled water was used for watering to avoid any contamination with impurities. The experiment was continued for 90 days from 29th October, 1972 to 25th January, 1973. Samples were periodically drawn from the pots at every interval of 15 days and the effects of nematocide on pH, electrical conductivity, nitrogen, phosphorus, potassium, organic matter and calcium carbonate were measured. The effects of the pesticide on the above parameters did not show any wide and marked differences in the case of the two soils and hence for the sake of brevity only the results for black cotton soil are given below in detail.

pH

For measuring the pH, an Elico pH meter model Li-10 with glass and saturated calomel electrode assembly was used. The pH was recorded in 1:2 soil water suspensions. The results obtained are recorded in table LIX and represented in Fig.21.

ELECTRICAL CONDUCTIVITY

For measuring the electrical conductivity a Philips conductivity meter with dip type cell was used. The conductivity was measured at 27 ± 1°C in 1:2 soil water suspensions. The results obtained are recorded in table IX and represented in Fig.22.

ORGANIC MATTER

Organic matter was estimated as per Walkey and Black's method[13].

Reagents: N/2 ferrous ammonium sulphate, N potassium dichromate, 96% conc. sulphuric acid, 85% phosphoric acid and diphenyl amine indicator solution. All the reagents used were of pure grade. The solutions were prepared in double distilled water.

Procedure: For the determination of organic matter 2 grams each of the soil samples were taken in 500 ml conical flasks. These were treated with 20 ml conc. sulphuric acid and 10 ml of N potassium dichromate solution. The flasks were shaken well for a minute or two and allowed to stand on an asbestos sheet, for about 30 minutes. Then 200 ml of water, 10 ml of phosphoric acid and 1 ml of diphenylamine indicator were added to every sample. A deep violet colour appeared. These were then titrated with N/2 ferrous ammonium sulphate solution till the violet colour changed to purple and finally to green. In the same way a blank determination was carried out. The organic carbon (uncorrected) was calculated using the following expression,

$$\text{Organic carbon (in grams)} = \frac{(\text{Blank titre} - \text{actual titre}) \times 0.003 \times M}{\text{Weight of the dry soil in grams}}$$

where M was the concentration of ferrous ammonium sulphate. The value of organic carbon was converted to organic matter by multiplying with a factor (1.724). The results obtained are recorded in table LXI and represented in Fig.23.

AVAILABLE NITROGEN

Available nitrogen was determined as per alkaline permanganate method[14].

Reagents: 0.32% potassium permanganate solution, 2.5% sodium hydroxide, N/50 sulphuric acid, N/50 sodium hydroxide and methyl red indicator. All the reagents were of pure grade and prepared in double distilled water.

Procedure: In a Kjeldahl flask 10 grams of each of the soil samples, along with 10 ml of distilled water, 50 ml of 0.32% potassium permanganate solution and 50 ml of 2.5% sodium hydroxide were taken. The flasks were then immediately fitted to the distillation apparatus. The end of the delivery tube of distillation apparatus was dipped into 10 ml of N/50 sulphuric acid solution taken in a conical flask. The ammonia gas which distilled over from the distillation flask was collected in a flask containing 20 ml of standard sulphuric acid. The excess of the sulphuric acid was titrated against N/50 sodium hydroxide solution using methyl red as indicator. Available nitrogen was calculated from the volume of sulphuric acid used up by the relation 1 ml of N/50 sulphuric = 2.8 mg nitrogen. The results are

recorded in table LXII and represented in Fig.24.

AVAILABLE PHOSPHORUS

Available phosphorus was determined as per Olsen's method[15].

Reagents: 0.5M sodium bicarbonate of pH 8.5, Darco-G 60 phosphorus free charcoal, ammonium molybdate solution containing 1.50 gm ammonium molybdate plus 100 C.C. of 32/N HCl and 5 ml of conc. HCl, stannous chloride solution (10 gm $SnCl_2.2H_2O$ in 25 ml conc. hydrochloric acid, diluted to 1320 ml) and phosphorus standards.

Procedure: In 150 ml conical flasks 5 grams of the soil samples were taken and a teaspoon of carbon black was added in each case. To each of the samples 100 ml of 0.5M $NaHCO_3$ solution was added. Contents of flasks were shaken for 30 minutes on a mechanical shaker and then filtered through Whatman filter paper number 42.

In 25 ml measuring flasks 5 ml of the clear soil extracts were taken and 5 ml of ammonium molybdate solution added in each case. The sides of the flasks were washed with distilled water. Solutions were shaked thoroughly and 1 ml of stannous chloride added in every case and volume made upto the mark. A blue colour developed. In the same way a blank was prepared. The absorbance of the solutions was recorded with the help of Bausch and Lomb spectronic '20' at a wavelength of 660 mμ using a red filter. Earlier a standard curve of phosphorus was prepared in the concentration range of 0 to 25 ppm vide figure 25, curve 1. The results for available phosphorus content were then evaluated from the standard curve and are given in

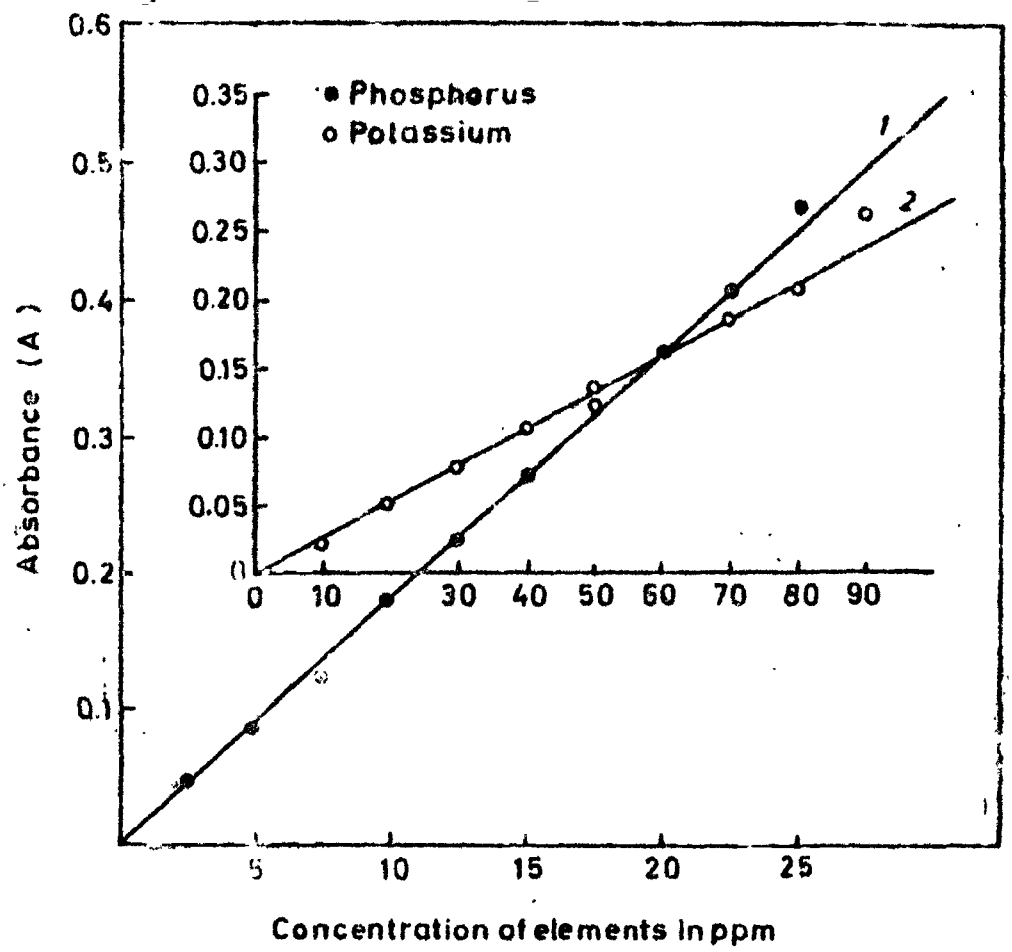

Fig.25 : tandard curves for P & K using spectrophotometric technique

table LXIII and represented in Fig.26.

AVAILABLE POTASSIUM

Available potassium was determined as per turbidity method[16].

Reagents: Morgan's reagent (100 gm sodium acetate plus 500 ml distilled water plus 30 ml of glacial acetic acid, made up to one l litre with distilled water); alcohol mixture containing equal volumes of isopropyl alcohol and methyl alcohol; sodium cobaltinitrite solution containing 50 gm cobalt nitrate plus 300 gm of sodium nitrite plus 25 ml of glacial acetic acid made up to one litre with distilled water and potassium standards.

Procedure: To 5 grams of each of the soil samples taken in 100 ml conical flasks 25 ml of morgan's reagent was added. The conical flasks were shaken for 5 minutes and the contents filtered through Whatman filter paper number 42.

A mixture of 2 ml of alcohol plus 6 drops of sodium cobaltinitrite solution was taken in several test tubes. To each one of them, 2 ml of the above soil extracts were added and the volume made upto 10 ml with Morgan's reagent. The solutions were shaken vigorously for 20 seconds and kept in ice cold bath. The temperature throughout the experiment was kept below 20°C by using an ice cold bath. A uniform turbidity developed. A blank was run in the same way using 2 ml of Morgan's reagent. For measurement of the absorbance of turbidity Bausch and Lomb spectronic '20' at a wavelength of 660 mμ with red filter was used. Earlier a standard curve of

potassium was prepared in the concentration range 0-90 ppm vide figure 25, curve 2. The results evaluated for available potassium from the standard curve are given in table LXIV and represented in Fig.27.

CALCIUM CARBONATE

Calcium carbonate was estimated by Piper's methods[17].

Reagents: N sodium hydroxide, N hydrochloric acid and bromothymol blue indicator.

Procedure: In 150 ml conical flasks, 5 grams of each of the soil samples were taken. To each sample 100 ml of N hydrochloric acid was added, shaken vigorously and allowed to stand for an hour.

10 ml of the above supernatants were then taken in 100 ml beakers and titrated against N sodium hydroxide solution using bromothymol blue indicator. The percentage of calcium carbonate was then calculated. The results obtained are recorded in table LXV.

STATISTICAL ANALYSIS

The experimental data obtained in case of each constituent of the soil was subjected to statistical analysis of variance according to the two way classification with one observation per cell, the null hypothesis being the equality of the effects of different levels of doses and different time intervals. The calculations were

done as follows:

(a) The correction factors was obtained from the formula

$$C.F. = \frac{(\text{Grand totals of readings})^2}{\text{No. of observations}}$$

(b) T.S.S. = Total of all squares - C.F.

(c) S.S. for days = Average of the squares of sum of readings of the constituent during total number of days - C.F.

(d) S.S. for doses = Average of the squares of sum of readings of the constituent during total number of doses - C.F.

(e) S.S. for error = T.S.S. - S.S. for days - S.S. for doses.

(f) M.S. (Mean square) = Variance = $\frac{S.S.}{D.F.}$,

where D.F. = degree of freedom or number of observations -1.

(g) L.S.D. (Least significant difference) =

$$\sqrt{\frac{\text{Error of the M.S. x 2}}{\text{D.F. of the days or doses}}} = t \text{ at } 5\%$$

(h) Variance ratio = $\frac{\text{M.S. for days or doses}}{\text{M.S. for error}}$

TABLE LVIII A

Physico-chemical characteristics of the black cotton and sodic saline soil

Soil sample	pH	Electrical conductivity in mhos cm^{-1}	Available nitrogen	Available phos-phorus	Available potassium	Organic matter	Calcium carbonate
Black cotton soil from Kota	8.05	6.30×10^{-4}	0.0056%	0.0012%	0.0075%	0.68%	3.5%
Aligarh soil type III (Sodic saline)	9.31	26.3×10^{-4}	0.0028%	0.0006%	0.0053%	0.29%	6.0%

TABLE LVIII B

Physico-chemical characteristics of the black cotton and sodic saline soil

Soil sample	Sand	Silt	Clay	C.E.C. Meq. per 100 g soil
Black cotton soil from Kota	8.4%	47.0%	44.8%	31.5
Aligarh soil type III (Sodic saline)	40.1%	49.9%	9.8%	10.8

TABLE LIX

Effect of D-D mixture on the pH of the black cotton soil

Dosage per 1 kg soil	pH of the treated soil at the end of							
	0 day	15 days	30 days	45 days	60 days	75 days	90 days	Average
0.0 C.C.	8.05	8.06	8.35	8.10	8.15	7.95	8.10	8.11
0.25 C.C.	8.05	8.10	8.50	8.20	8.20	7.95	8.15	8.15
0.50 C.C.	8.05	8.10	8.45	8.20	8.20	7.95	8.10	8.15
0.75 C.C.	8.05	8.10	8.40	8.25	8.25	7.95	8.10	8.16
1.00 C.C.	8.05	8.10	8.35	8.20	8.20	8.10	8.10	8.16
1.25 C.C.	8.05	8.10	8.35	8.20	8.20	8.95	8.10	8.13
Average	8.05	8.09	8.40	8.19	8.20	8.14	8.11	

TABLE LX

Effect of D-D mixture on the electrical conductivity of the black cotton soil

Dosage per kg soil	Electrical conductivity in mhos per cm x 10^{-4} of the treated soil at the end of							
	0 day	15 days	30 days	45 days	60 days	75 days	90 days	Average
0.00 C.C.	6.27	5.33	4.10	4.75	5.18	4.18	5.26	5.01
0.25 C.C.	5.90	4.10	3.63	4.60	4.75	4.04	5.11	4.59
0.50 C.C.	5.90	4.10	3.70	4.28	4.85	3.99	4.85	4.52
0.75 C.C.	5.90	4.22	3.62	4.12	4.86	3.62	5.19	4.50
1.00 C.C.	6.28	4.27	3.75	3.72	4.65	4.17	4.78	4.52
1.25 C.C.	6.28	4.92	3.80	4.09	5.05	4.09	5.06	4.74
Average	6.09	4.49	3.43	4.26	4.89	4.02	5.04	

TABLE LXI

Effect of D-D mixture on the decomposition of organic matter of black cotton soil

Dosage per kg soil	Organic matter in mg per 100 gm soil at the end of							
	0 day	15 days	30 days	45 days	60 days	75 days	90 days	Average
0.00 C.C.	678.9	700.5	760.8	784.5	752.1	730.1	706.9	730.4
0.25 C.C.	685.3	715.5	771.5	775.9	740.7	717.7	700.5	729.6
0.50 C.C.	685.3	700.5	756.5	758.6	722.0	708.7	698.3	718.5
0.75 C.C.	685.4	702.6	752.1	756.5	715.5	702.9	686.3	714.5
1.00 C.C.	685.4	687.5	748.9	750.0	704.7	700.5	691.8	709.8
1.25 C.C.	685.4	681.2	743.4	741.3	698.4	687.5	683.5	703.0
Average	684.3	698.0	755.5	761.2	722.2	707.9	695.5	

TABLE LXI

Effect of D-D mixture on the decomposition of organic matter of black cotton soil

Dosage per kg soil	Organic matter in mg per 100 gm soil at the end of							
	0 day	15 days	30 days	45 days	60 days	75 days	90 days	Average
0.00 C.C.	679	701	761	785	752	730	707	730
0.25 C.C.	685	716	772	776	741	718	701	730
0.50 C.C.	685	701	757	759	722	709	698	719
0.75 C.C.	685	703	752	757	716	703	686	715
1.00 C.C.	685	688	749	750	705	701	692	710
1.25 C.C.	685	681	743	741	698	688	684	703
Average	684	698	756	761	722	708	696	

TABLE LXII

Effect of D-D mixture on the availability of nitrogen of black cotton soil

Dosage per kg soil	Available nitrogen in mg per 100 gm soil at the end of							
	0 day	15 days	30 days	45 days	60 days	75 days	90 days	Average
0.00 C.C.	5.60	12.04	15.44	15.40	14.32	13.48	13.20	12.78
0.25 C.C.	5.60	13.03	15.66	16.28	14.37	13.58	13.16	13.27
0.50 C.C.	5.60	13.37	17.51	16.52	14.14	13.30	13.16	13.37
0.75 C.C.	5.60	13.62	17.17	16.66	14.14	13.25	12.70	13.31
1.00 C.C.	5.60	12.83	15.54	15.16	13.81	13.39	12.40	12.68
1.25 C.C.	5.60	12.83	15.54	15.07	13.58	12.55	12.18	12.62
Average	5.60	12.95	16.31	15.85	14.06	13.26	12.80	

TABLE LXIII

Effect of D-D mixture on available phosphorus of black cotton soil

Dosage per kg soil	Available phosphorus in mg per 100 gm soil at the end of							
	0 day	15 days	30 days	45 days	60 days	75 days	90 days	Average
0.00 C.C.	1.20	1.99	2.03	1.40	1.33	1.33	1.16	1.49
0.25 C.C.	1.15	2.00	2.16	1.50	1.26	1.23	1.20	1.50
0.50 C.C.	1.15	2.10	2.30	1.70	1.48	1.30	1.20	1.60
0.75 C.C.	1.15	2.20	2.46	1.72	1.50	1.40	1.30	1.67
1.00 C.C.	1.15	1.98	2.15	1.60	1.30	1.26	1.20	1.52
1.25 C.C.	1.15	1.98	2.15	1.46	1.23	1.16	1.13	1.46
Average	1.16	2.04	2.37	1.56	1.37	1.28	1.20	

TABLE LXIV

Effect of D-D mixture on available potassium of black cotton soil

Dosage per kg soil	Available potassium in mg per 100 gm soil at the end of							
	0 day	15 days	30 days	45 days	60 days	75 days	90 days	Average
0.00 C.C.	7.50	13.41	14.50	14.08	13.33	12.33	11.33	12.35
0.25 C.C.	7.50	13.25	13.58	12.91	12.83	11.91	11.08	11.86
0.50 C.C.	7.50	12.66	13.41	12.58	11.33	11.41	10.91	11.40
0.75 C.C.	7.50	12.58	13.08	12.58	11.41	11.33	10.45	11.27
1.00 C.C.	7.50	13.08	13.91	13.58	12.66	11.58	11.08	11.91
1.25 C.C.	7.50	13.25	13.58	13.91	12.58	12.00	11.33	12.09
Average	7.50	13.04	13.68	13.27	12.35	11.76	11.03	

TABLE LXV

Effect of D-D mixture on calcium carbonate of black cotton soil

Dosage per kg soil	Calcium carbonate in gm per 100 gm soil at the end of							
	0 day	15 days	30 days	45 days	60 days	75 days	90 days	Average
0.00 C.C.	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
0.25 C.C.	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
0.50 C.C.	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
0.75 C.C.	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
1.00 C.C.	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
1.25 C.C.	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
Average	3.5	3.5	3.5	3.5	3.5	3.5	3.5	

RESULTS AND DISCUSSION

The influence of D-D mixture on pH, electrical conductivity, organic matter, available nitrogen, phosphorus, potassium and calcium carbonate content of black cotton soil is expressed in tables LIX to LXV and Figs.21 to 27. Each datum in a table represents a mean of three values recorded at 0, 15, 30, 45, 60, 75 and 90 days after application of the fumigant. Similarly the average values for different days represent a mean of several values obtained at different doses viz. ⊙ 0.0, 0.25, 0.50, 0.75, 1.00 and 1.25 ml per kg soil. The results were subjected to statistical analysis of variance according to the two way classification and LSD values were calculated using the value of t at 5% level of significance. A summary of the results on the effect of D-D mixture on nutrient availability in black cotton soil with reference to organic matter, nitrogen, phosphorus and potassium is represented vide table LXXII and that in case of sodic saline soil vide table LXXIII. In the discussion that follows, only the average values for doses and days have been considered and the term significant is used as meaning statistically significant at 5% F level (2.52 for doses and 2.42 for days).

EFFECT ON pH

The data on pH vide table LIX were subjected to statistical analysis of variance. It gave results as given in table LXVI. A reference to figure 21 and the data of tables LIX and LXVI indicated that D.D. mixture had no marked influence on the pH value of the

TABLE LXVI

Statistical analysis of variance of the pH data of black cotton soil

C.F. = $\frac{(342.11)^2}{42}$ = 2786.6480

T.S.S. = 2787.3811 - 2786.6480 = 0.7331

S.S. for days = 2787.3218 - 2786.6480 = 0.6738

S.S. for doses = 2786.6633 - 2786.6480 = 0.0153

S.S. for error = 0.7331 - 0.6738 - 0.0153 = 0.0440

Source of variation	D.F.	S.S.	M.S.	Variance ratio	F	
					5%	1%
Days	6	0.6738	0.1123	74.86660	2.42	3.47
Doses	5	0.0153	0.0031	0.00206	2.52	3.70
Error	30	0.0440	0.0015			
Total	41					

L.S.D. for days = $\sqrt{\frac{0.0015 \times 2}{6}} \times 2.042 = \sqrt{0.0005} \times 2.042 = 4.5 \times 10^{-2}$

L.S.D. for doses = $\sqrt{\frac{0.0015 \times 2}{5}} \times 2.042 = \sqrt{0.0006} \times 2.042 = 5.0 \times 10^{-2}$

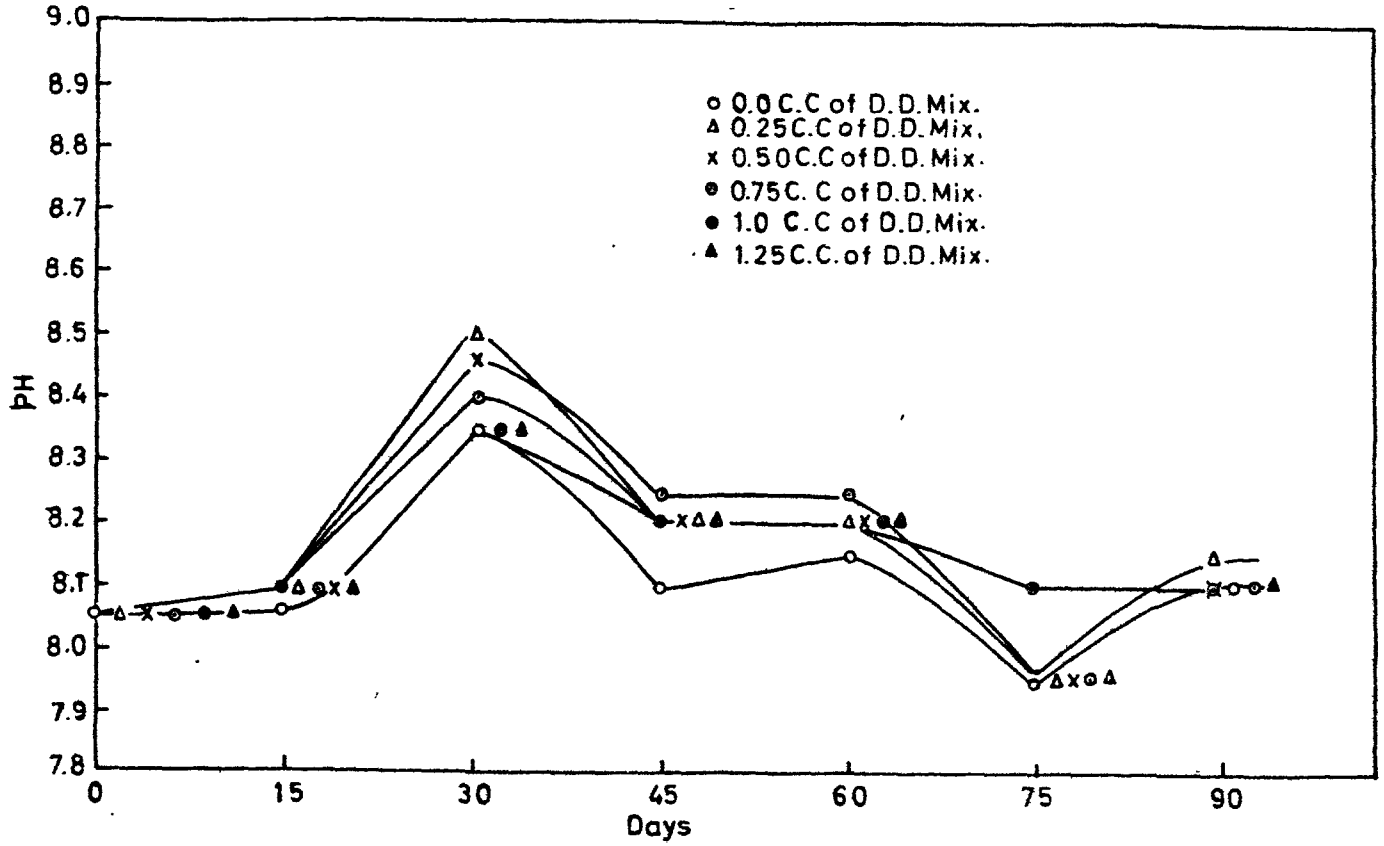

Fig. 21 Effect of D.D. Mix. on PH of a black cotton soil at different intervals of time

soils. The effect was statistically insignificant. The influence with passage of time was, however, significant. The pH increased upto 30 days and thereafter declined. This effect was very small.

EFFECT ON ELECTRICAL CONDUCTIVITY

The data on electrical conductivity vide table LX were subjected to statistical analysis of variance. It gave results as given in table LXVII. A reference to figure 22 and the data of tables LX and LXVII indicated that D-D mixture had no marked influence on electrical conductivity in case of black cotton soil as well as sodic saline soil and the effect was statistically insignificant both for doses and days. The value declined, reached a minimum at 30 days after application and rose again. The application of the nematocide probably resulted in fixation of certain ions like potassium in the soils in the early stages. Later, a declining fixing effect was observed probably as a result of the decomposition of the pesticide in the soil medium.

EFFECT ON ORGANIC MATTER

The data on organic matter vide table LXI were subjected to statistical analysis of variance. It gave results as given in table LXVIII.

A reference to figure 23 and the data incorporated in tables LXI and LXVIII showed that as compared to the control, the amount of organic matter significantly decreased with increasing applications of the fumigant. With passage of time, however, it significantly increased, though still below the control, reached a

TABLE LXVII

Statistical analysis of variance of data on electrical conductivity of black cotton soil

C.F. = $\frac{(195.31)^2}{42}$ = 908.2380

T.S.S. = 978.0097 - 908.2380 = 69.7717

S.S. for days = 930.08410 - 908.2380 = 21.8461

S.S. for doses = 909.6314 - 908.2380 = 1.3934

S.S. for error = 69.7717 - 21.8461 - 1.3934 = 46.5322

Source of variation	D.F.	S.S.	M.S.	Variance ratio	F	
					5%	1%
Days	6	21.8461	3.6410	2.3473	2.42	3.47
Doses	5	1.3934	0.2787	0.1796	2.52	3.70
Error	30	46.5322	1.5511			
Total	41					

L.S.D. for days = $\sqrt{\frac{2 \times 1.5511}{6}} \times 2.042 = \sqrt{0.5170} \times 2.042 = 1.5$

L.S.D. for doses = $\sqrt{\frac{2 \times 1.5511}{5}} \times 2.042 = \sqrt{0.6204} \times 2.042 = 1.6$

TABLE LXVIII

Statistical analysis of variance of data on organic matter of black cotton soil

C.F. = $\frac{(30141.8)^2}{42}$ = 21631621.60

T.S.S. = 21670691.54 - 21631621.60 = 39069.94

S.S. for days = 21664497.36 - 21631621.60 = 32875.76

S.S. for doses = 21635820.97 - 21631621.60 = 4199.37

S.S. for error = 39069.94 - 32875.76 - 4199.37 = 1994.81

Source of variance	D.F.	S.S.	M.S.	Variance ratio	F	
					5%	1%
Days	6	32875.76	5479.293	82.40	2.42	3.47
Doses	5	4199.37	839.874	12.63	2.52	3.70
Error	30	1994.81	66.493			
Total	41					

L.S.D. for days = $\sqrt{\frac{2 \times 66.493}{6}} \times 2.042$ = 9.5

L.S.D. for doses = $\sqrt{\frac{2 \times 66.493}{5}} \times 2.042$ = 10.4

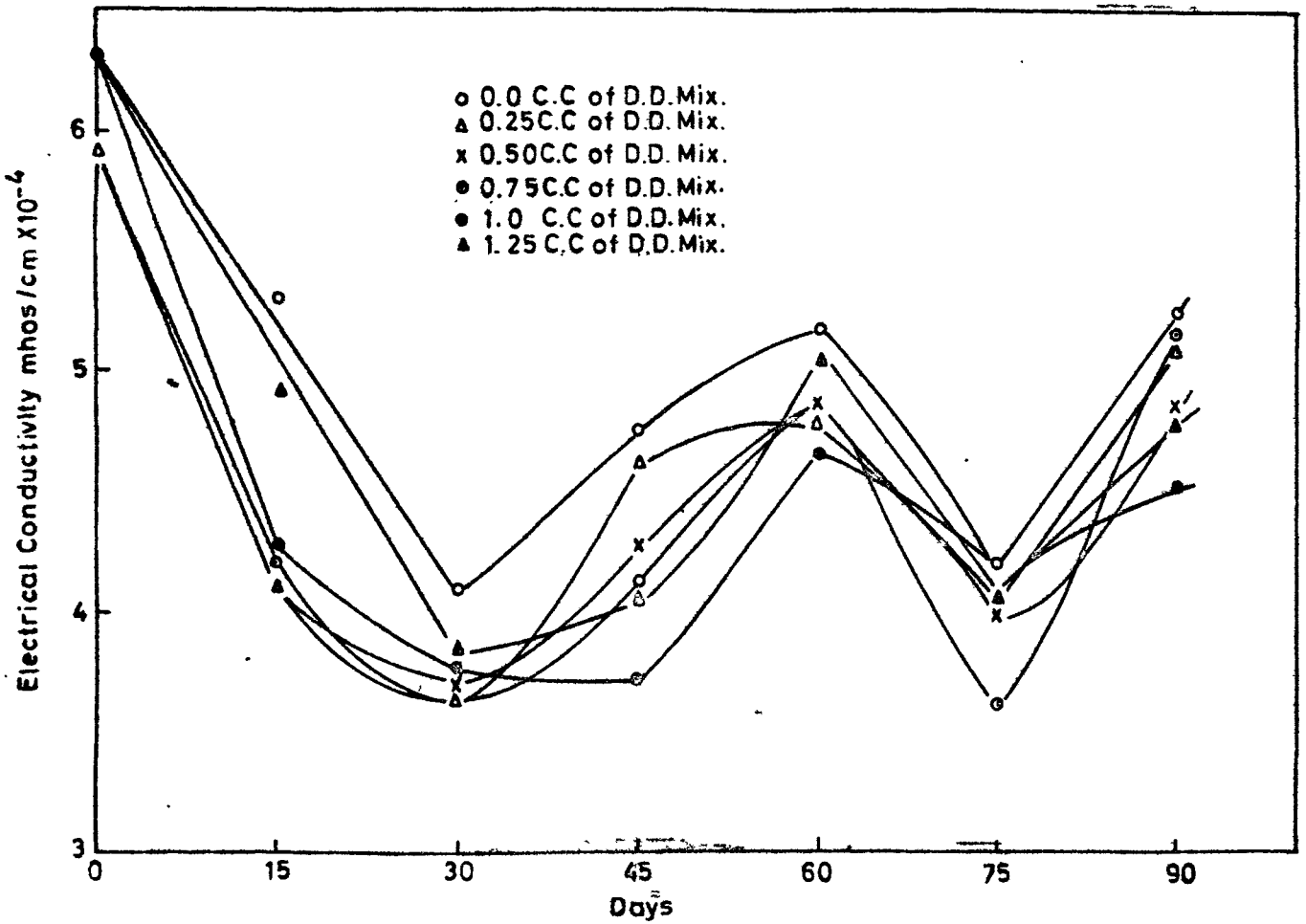

Fig. 22 Effect of the D.D.Mixture on electrical conductivity of a black cotton soil at different intervals of time

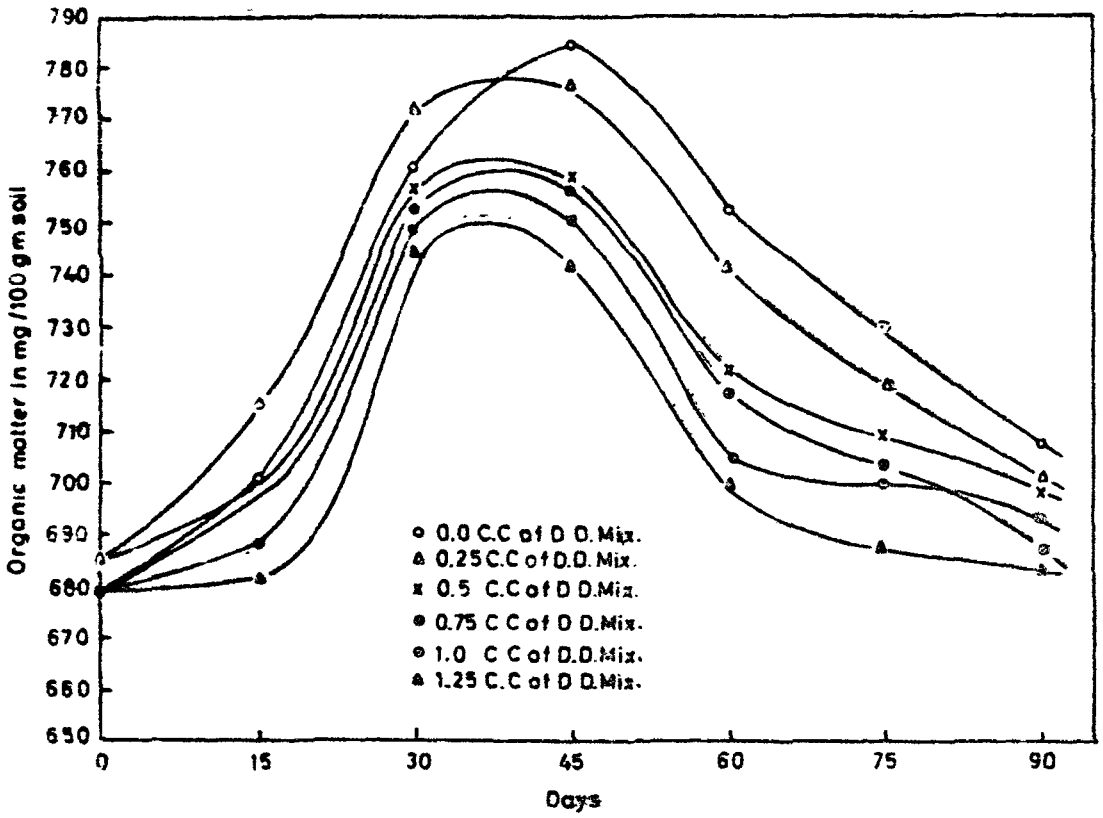

Fig 23 Effect of DD Mix on the decomposition of organic matter of a black cotton soil at different intervals of time

maximum at 45 days in case of black cotton soil and 30 days in sodic saline soil and then significantly declined. The evidence for the decline in organic matter is provided by the fact that while fumigants like D-D greatly eliminate nematode population, many soil bacteria are fairly resistant to fumigants. The eradicant-type chemicals produced greater re-invasion potentials[18] with the result that the reactivated soil organisms brought about a rapid decomposition of organic matter which significantly declined. Such effects have also been reported by Smith and Wenzel[19] as well as others in case of soils treated with chlorinated insecticides.

EFFECT ON AVAILABLE NITROGEN

The data on available nitrogen vide table LXII were subjected to statistical analysis of variance. It gave results as given in table LXIX. A reference to figure 24 and the data incorporated in tables LXII and LXIX showed that available nitrogen significantly increased upto an application of 0.50 ml of the fumigant per kg of soil in case of black cotton soil and 0.75 ml in case of sodic saline soil and upto 30 days. Thereafter a significant decline was observed in both cases.

The initial increase in available nitrogen was due to the decomposition of soil organic matter by fumigant resistant bacteria[18] which resulted in the release of nitrogen. The decrease with large doses on the other hand appeared to be due to the inhibitory effects of large doses of the fumigant on nitrification[20,21]. The decline with passage of time was due to the dissipation of the toxic chemical

TABLE LXIX

Statistical analysis of variance of data on available nitrogen of black cotton soil

C.F. = $\frac{(544.98)^2}{42}$ = 7071.5048

T.S.S. = 7532.2764 - 7071.5048 = 460.7716

S.S. for days = 7521.8497 - 7071.5048 = 450.3449

S.S. for doses = 7076.4725 - 7071.5048 = 4.9677

S.S. for error = 460.7716 - 450.3449 - 4.9677 = 5.4590

Source of variation	D.F.	S.S.	M.S.	Variance ratio	F 5%	F 1%
Days	6	450.3449	75.0575	412.4038	2.42	3.47
Doses	5	4.9677	0.9935	5.4588	2.52	3.70
Error	30	5.4590	0.18200			
Total	41					

L.S.D. for days = $\sqrt{\frac{2 \times 0.182}{6}} \times 2.042 = \sqrt{0.0607} \times 2.042 = 0.50$

L.S.D. for doses = $\sqrt{\frac{2 \times 0.182}{5}} \times 2.042 = \sqrt{0.0728} \times 2.042 = 0.53$

⊕ The effect of pesticidal chemicals on the availability of phosphorus has been discussed in detail by Alexander et.al.[1,2] who have reported the bacterial reduction of available phosphorus to unavailable phosphine as it is found in different oxidation states.

$$\underset{+5}{H_3PO_4} \xrightarrow{2H} \underset{+3}{H_3PO_3} \xrightarrow{2H} \underset{+1}{H_3PO_2} \xrightarrow{4H} \underset{-3}{PH_3}$$

(oxidation states)

However, further work is required to justify this conclusion.

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2. Singhal,J.P. and Singh,C.P. Pl.Soil, 46, 69, 1977.

and reinfestation of the high potential zones of the treated soil by the fast growing fungi of the vigorously competitive sugar- and amino acid utilising kinds[22].

EFFECT ON AVAILABLE PHOSPHORUS

The data on available phosphorus vide table LXIII were subjected to statistical analysis of variance. It gave results as given in table LXX. A reference to figure 26 and the data incorporated in tables LXIII and LXX revealed that the availability of phosphorus increased with applications of D-D mixture upto 0.75 ml/kg of soils and it reached a maximum value at 30 days. Higher doses and days reduced the availability. All the effects were statistically significant.

Wensley[23] and Martin et al.[24] have reported increased and highly stimulated microbial activity in soil as a result of fumigation. The action of ascomycetes, actinomycetes and the reinfested fungus flora resulted in the decomposition of soil organic matter bringing about a gradual increase in phosphorus availability till a peak was reached both with doses and time. However, the toxic effect of too high doses and certain chemical reactions like reduction of phosphorus to PH_3 with passage of time resulted in the decline of phosphorus.

EFFECT ON AVAILABLE POTASSIUM

The data on available potassium vide table LXIV were subjected to statistical analysis of variance. It gave results as given in

TABLE LXX

Statistical analysis of variance of data on available phosphorus of black cotton soil

C.F. = $\frac{(64.80)^2}{42}$ = 99.9771

T.S.S. = 106.7259 - 99.9771 = 6.7486

S.S. for days = 106.3667 - 99.9771 = 6.3896

S.S. for doses = 100.2038 - 99.9771 = 0.2267

S.S. for error = 6.7468 - 6.3896 - 0.2267 = 0.1305

Source of variation	D.F.	S.S.	M.S.	Variance ratio	F 5%	F 1%
Days	6	6.3896	1.0649	242.0250	2.42	3.47
Doses	5	0.2267	0.0453	10.2954	2.52	3.70
Error	30	0.1305	0.0044			
Total	41					

L.S.D. for days = $\sqrt{\frac{2 \times 0.0044}{6}} \times 2.042 = \sqrt{0.0015} \times 2.042 = 0.07$

L.S.D. for doses = $\sqrt{\frac{2 \times 0.0044}{5}} \times 2.042 = \sqrt{0.0017} \times 2.042 = 0.08$

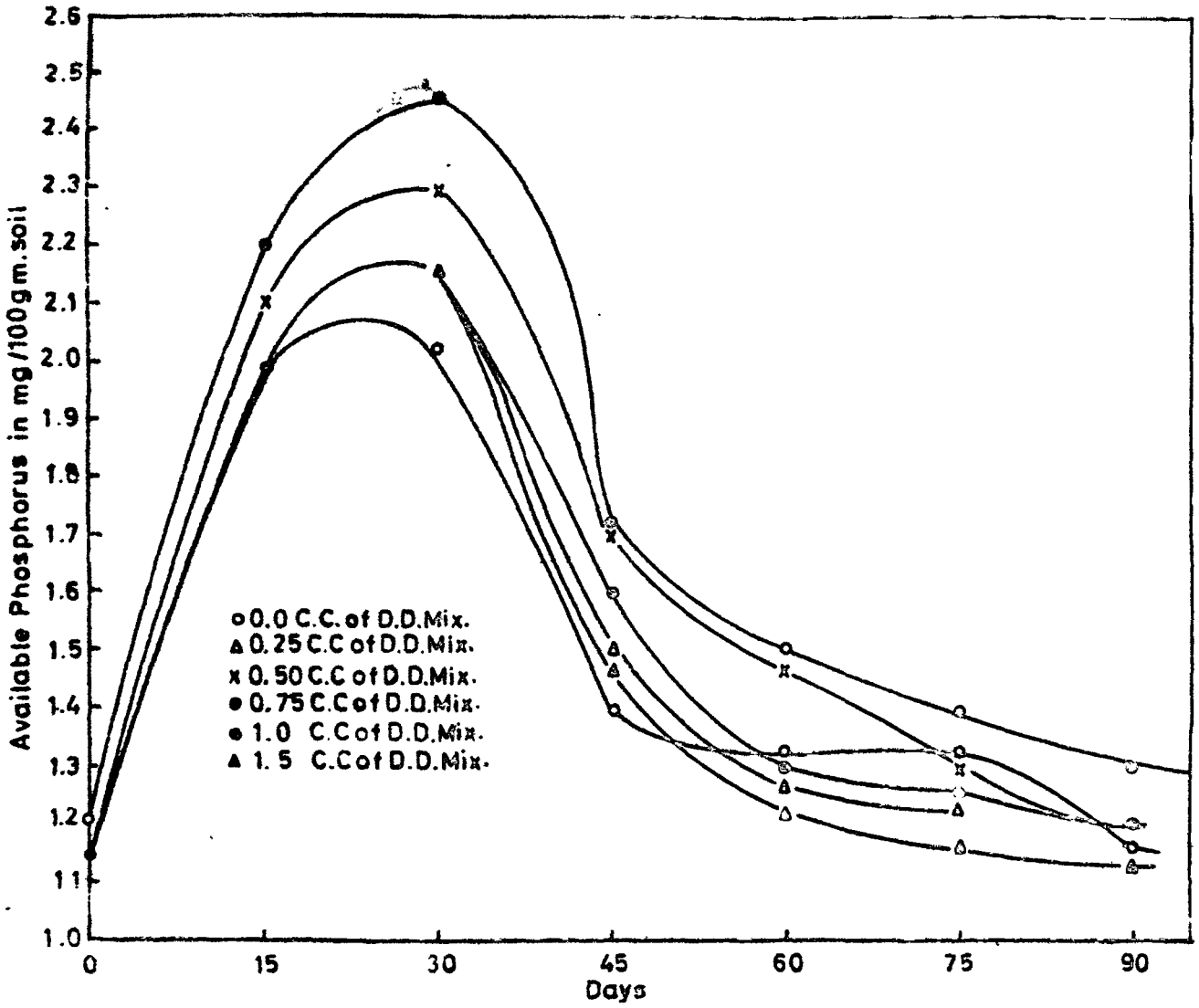

Fig. 26 Effect of D.D. Mix. on the availability of Phosphorus of a black cotton soil at different interval of time

The D-D mixture has powerful nematocidal properties and it affects the microbial population in soil with the result that there is a change in oxidation reduction potentials of the soil system and degradation of organic matter takes place. The release of carboxylic acids is reported and that might affect the $CaCO_3$ content therefore it is felt that there would be some effect of D-D mixture on $CaCO_3$ content of the soil.

table LXXI. A reference to figure 27 and the data incorporated in tables LXIV and LXXI showed that the effect of D-D on potassium availability generally decreased with increasing application of D-D mixture upto 0.75 ml per kg soil and thereafter increased. With passage of time it increased upto 30 days and thereafter followed a fluctuating pattern. The up and down trend with passage of time though statistically significant followed the trend of the control. At the most, therefore, it could be said that D-D had a slight suppressive influence on potassium availability in these soils. The mechanism by which this occurred was not entirely clear. Probably the fumigant had a tendency to fix available potassium into non-exchangeable form on the clay lattice but further work is required to justify this conclusion.

EFFECT ON CALCIUM CARBONATE

D-D mixture had no marked influence on calcium carbonate content of the soil as revealed by results reported in table LXV.

TABLE LXXI

Statistical analysis of variance of data on available potassium of black cotton soil

C.F. = $\frac{(495.81)^2}{42}$ = 2.042 = 0.0586 x 2.042 = .494

T.S.S. = 6021.3071 - 5853.0370 = 168.2701

S.S. for days = 6022.7586 - 5853.0370 = 159.7216

S.S. for doses = 5856.3120 - 5853.0370 = 3.2750

S.S. for error = 168.2701 - 159.7216 - 3.2750 = 5.2735

Source of variation	D.F.	S.S.	M.S.	Variance ratio	F 5%	F 1%
Days	6	159.7216	26.6202	151.4232	2.42	3.47
Doses	5	3.2750	0.6550	0.3725	2.52	3.70
Error	30	5.2735	0.1758			
Total	41					

L.S.D. for days = $\sqrt{\frac{2 \times 0.1758}{6}}$ x 2.042 = $\sqrt{0.0586}$ x 2.042 = 0.49

L.S.D. for doses = $\sqrt{\frac{2 \times 0.1758}{5}}$ x 2.042 = $\sqrt{0.0703}$ x 2.042 = 0.54

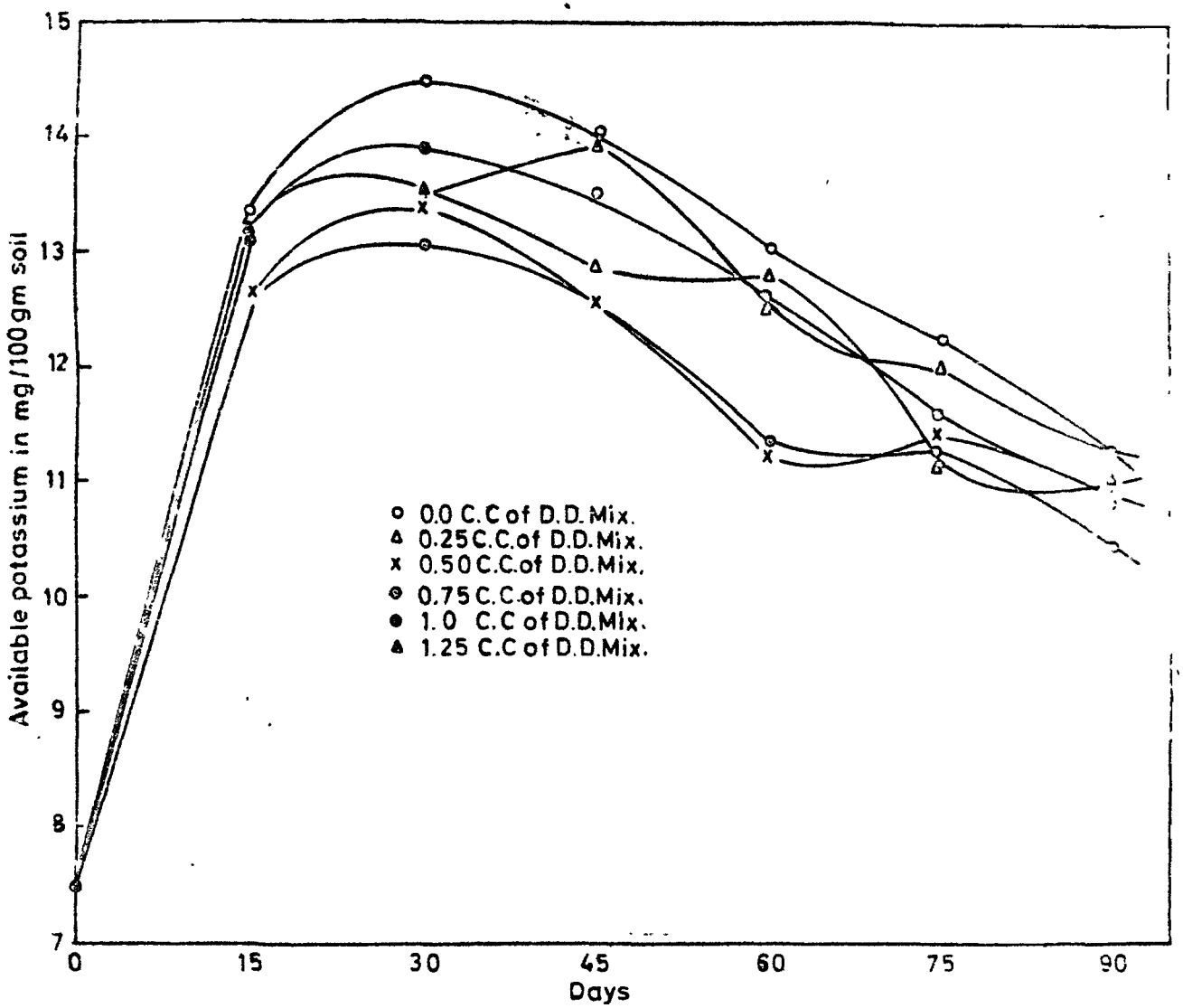

Fig 27 Effect of D.D. Mix. on the availability of Potassium of a black cotton soil at different intervals of time

TABLE LXXII

Effect of D-D mixture on nutrient availability of black cotton soil for different doses of the mixture at various intervals of time

Treatment Doses (in ml per kg of soil)/Duration (days)	Average values of available nutrients for various doses and days in mg per 100 g soil			
	Organic matter	Nitrogen	Phosphorus	Potassium
0.00	730.4	12.78	1.49	12.35
0.25	729.6	13.27	1.50	11.86
0.50	718.5	13.37	1.60	11.40
0.75	714.5	13.31	1.67	11.27
1.00	709.8	12.68	1.52	11.91
1.25	703.0	12.62	1.46	12.09
LSD	10.4	0.53	0.08	0.54
Variance ratio	12.6	5.45	10.29	0.37
0 day	684.3	5.60	1.16	7.50
15 days	698.0	12.95	2.04	13.04
30 days	755.5	16.31	2.37	13.68
45 days	761.2	15.85	1.56	13.27
60 days	722.2	14.06	1.37	12.35
75 days	707.9	13.26	1.28	11.76
90 days	695.5	12.80	1.20	11.03
LSD	9.5	0.50	0.07	0.49
Variance rato	82.4	412.40	242.02	151.42

TABLE LXXIII

Effect of D-D mixture on nutrient availability of sodic saline soil for different doses of the mixture at various intervals of time

Treatment Doses (in ml per kg of soil)/Duration (days)	Average values of available nutrients for various doses and days in mg per 100 g soil			
	Organic matter	Nitrogen	Phosphorus	Potassium
0.0	337.1	7.19	0.72	11.17
0.5	336.2	7.45	0.97	10.55
1.0	331.1	7.75	0.94	10.15
1.5	328.1	7.03	0.94	9.99
2.0	322.1	7.38	0.85	10.92
2.5	315.8	7.06	0.78	10.98
LSD	9.1	0.37	0.09	0.58
Variance ratio	9.4	7.82	9.66	7.85
0 day	294.1	8.80	0.60	5.25
15 days	335.1	8.71	0.95	10.72
30 days	358.5	9.42	1.12	13.41
45 days	355.0	8.55	1.03	13.17
60 days	328.1	7.88	0.79	10.81
75 days	316.7	7.55	0.74	11.01
90 days	311.7	7.18	0.68	10.02
LSD	8.3	0.34	0.09	0.53
Variance ratio	65.1	334.59	42.75	215.42

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Adsorption of nicotine on dickite

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STUDIES ON THE THERMODYNAMICS OF ZINC EXCHANGE IN MONTMORILLONITE

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The ion exchange equilibria and mechanism of Zn exchange with Na montmorillonite has been studied with the help of adsorption isotherms and thermodynamic parameters. The exchange isotherms, K and ΔG^0 values indicated a spontaneity of reaction and a higher preference of Zn for the montmorillonite surface. A stronger binding of Zn and changes in the hydration rates of Zn and Na with increase in order were suggested by enthalpy and entropy effects respectively. The surface phase activity coefficients and the excess thermodynamic functions were indicative of a nonideal heterogeneous exchange in which the mixture of ions on the montmorillonite surface was more stable and more tightly bound with significant differences in the hydration rates of the ions in the mixture with respect to the homo-ionic forms.

The adsorption of Zn and its reactions with clays and soils are receiving increasing attention. Zn deficiencies are common in plants growing on sodic soils. The process of ion exchange is important in plant nutrition. The cation exchange of Zn on montmorillonite as well as its exchange adsorption on soils have been studied by several workers (ELGABLY and JENNY, 1943; JURINAK and BAUER, 1956). In the study of ion exchange it has been noticed that although two ions may exchange stoichiometrically, they would not, in general, be preferred or bound equally strongly on a surface. In view of the importance of the nature of ion exchange, the exchange of Zn with Na-montmorillonite has been studied with the help of thermodynamic models of GAINES and THOMAS (1953), EL-SAYED *et al.* (1970), and SINGHAL and SINGH (1973). It has been felt that such a study will be of considerable significance in understanding the mechanism of zinc interaction with Na-montmorillonite, a clay mineral which occurs widely in montmorillonitic sodic soils.

MATERIALS AND METHODS

The montmorillonite clay used in these studies was extracted from a Mississippi bentonite which was obtained from Ward's Natural Science Establishment, Rochester, New York. The suspension obtained by removal of organic matter and sedimentation was saturated several times with 1N NaCl and then centrifuged and washed to give less than two micron chloride-free Na-montmorillonite suspension. The concentration of the suspension was 14.6 g per litre.

For the determination of the cation exchange capacity of Na-montmorillonite (Na-CEC) a known volume of the suspension was treated with a mixture consisting of 1N $CaCl_2$ in 0.1N HCl and then estimating the amount of Na released (JACKSON, 1958). The value as calculated came out to be 90 meq. per 100 g clay.

For determination of time of exchange equilibrium at constant ionic strength three sets of 10 ml suspensions of Na-montmorillonite were treated with 1, 6, and 15 ml of 0.02N $Zn(NO_3)_2$ and 14, 9, and 0 ml of 0.03N $NaNO_3$ solutions respectively. The mixtures were shaken for 1 hr. Similar exchanges were carried out at 3, 6, and 9 hr also. At the end of the above specified time intervals the mixtures were centrifuged and Zn was estimated in the supernatant liquids by titration with a standard solution of EDTA. The amount of Zn exchanged at different time intervals was then obtained from the amount of Zn added minus Zn remaining in the supernatants. The results are illustrated by Fig. 1, curves 1–3. A time of 3 hr was found to be sufficient for attainment of equilibrium during the exchange.

Cation exchange in clays is also controlled by pH. For determination of pH suitable to carry out exchange studies, two sets of 10 ml suspensions of Na-montmorillonite were treated with 0.1N HNO_3 and 0.1N NaOH to obtain the desired levels of pH. Zinc exchange was then carried out at a constant ionic strength by shaking the mixtures with variable and required volumes of $Zn(NO_3)_2$ and Na-montmorillonite at a temperature of 30°C and a time of 3 hr. The results of the pH effect on exchange are recorded in Fig. 2, curves 1 and 2.

Since exchange of Zn with Na-montmorillonite was found to be unaffected by variation of pH from 4.5 to 6, the exchange isotherms were determined at pH = 5.0. This also avoided hydroxide precipitation. Ten ml samples of Na-montmorillonite were taken in a large number of glass-stoppered tubes and their pH adjusted to 5.0 by

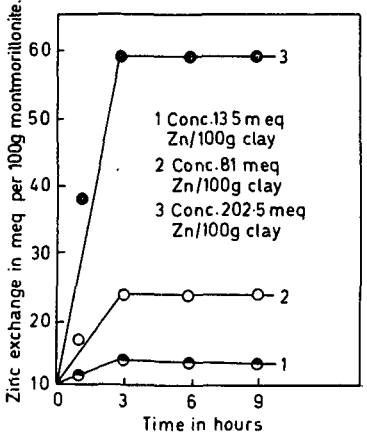

Fig. 1. Effect of time on the adsorption of zinc by sodium montmorillonite at 30°C.

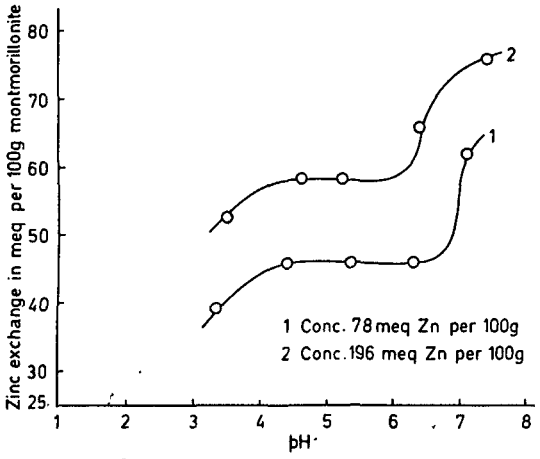

Fig. 2. Effect of pH on the adsorption of zinc by Na-montmorillonite at 30°C.

adding 0.1N HNO_3. The suspensions were then treated with various but proportionate amounts of 0.02N $Zn(NO_3)_2$ and 0.03N $NaNO_3$ to provide a constant ionic strength and a constant volume (25 ml) for the exchange. The tubes were shaken at 30 ± 0.1°C in the first set of experiments and 60 ± 0.1°C in the second set for 3 hr in a thermostatic water bath. The mixtures were then immediately centrifuged, and Na and Zn estimated in the supernatants by flame photometry and titration with a standard solution of EDTA, respectively. The corresponding concentration of Na in the clay phase was obtained by subtraction of Na concentration in the supernatant from Na-CEC. Similarly the amount of Zn taken up by the clay surface in replacing Na was obtained by difference between the amount of Zn added and the amount of Zn left behind in the equilibrium suspension.

RESULTS AND DISCUSSION

The reaction between Zn ions in solution and Na ions on the montmorillonite surface can be represented by the equation:

$$\bar{C}_{Na}+C_{Zn} \rightleftharpoons C_{Na}+\bar{C}_{Zn}. \quad (1)$$

The concentrations of the ions concerned, in terms of equivalent ionic fractions, were calculated from the following expressions:

$$\bar{X}_{Zn}=\frac{\bar{C}_{Zn}}{\quad} \quad X_{Zn}=\frac{C_{Zn}}{\quad} \quad \bar{C}_{Na} \quad C_{Na}$$

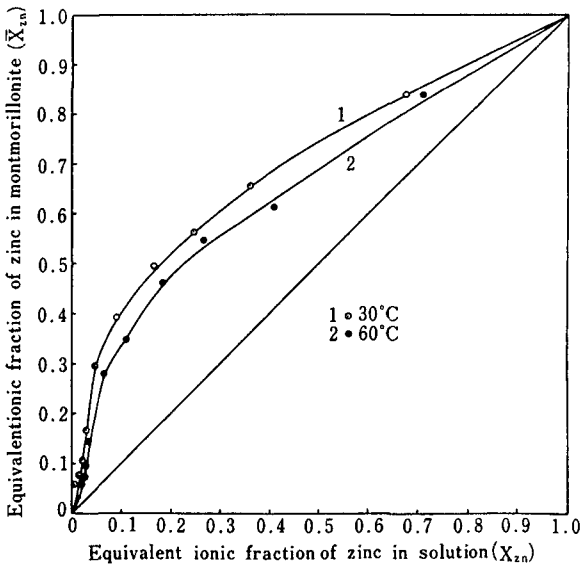

Fig. 3. Exchange isotherms for zinc ion on Na-montmorillonite.

where $\bar{C}$ was the total ion concentration in the clay phase and C that in the solution. The values obtained for the equivalent ionic fractions at 30 and 60°C were plotted and the exchange isotherms obtained are given in Fig. 3.

Isotherms at both the temperatures were found to deviate from the diagonal indicating that at constant ionic strength Zn continuously replaced Na from the montmorillonite surface over the entire range of concentrations studied by us and that it had a higher preference for the clay surface than Na. The preference also varied with temperature, being higher at 30 than at 60°C.

For a further examination of the exchange behaviour in dilute montmorillonite suspensions the separation factors and selectivity coefficients (HELFFERICH, 1962) were calculated from the following respective expressions:

$$\alpha^{Zn}_{Na}=\left(\frac{\bar{X}_{Zn}}{\bar{X}_{Na}}\right)\left(\frac{X_{Na}}{X_{Zn}}\right). \qquad (2)$$

Correcting the separation factor for interactions in the solution phase by introducing the factor

$$K_C=\frac{(\bar{X}_{Zn})}{(\bar{X}_{Na})^2}\ \frac{(X_{Na}\,y_{Na})^2}{(X_{Zn}\,y_{Zn})}, \qquad (3)$$

where y_{Na} and y_{Zn} were the activity coefficients of the two ions in the solution phase. The values are given in Table 1. A plot of the effect of Zn concentration on selectivity

... for the Zn exchange on Na-montmorillonite.

$\bar{X}_{Zn}$	X_{Zn}	$\bar{X}_{Na}$	X_{Na}	K_C	log K_C
		(Set 30°C)			
0.058	0.004	0.942	0.996	14.1	1.15
0.075	0.014	0.925	0.986	5.4	0.73
0.107	0.023	0.893	0.977	5.0	0.70
0.166	0.026	0.834	0.974	7.8	0.89
0.299	0.048	0.701	0.952	10.6	1.02
0.395	0.091	0.605	0.909	9.2	0.97
0.499	0.164	0.501	0.836	8.2	0.91
0.562	0.250	0.438	0.750	6.6	0.82
0.650	0.366	0.350	0.633	6.0	0.77
0.843	0.677	0.157	0.322	5.6	0.75
		(Set 60°C)			
0.060	0.004	0.940	0.996	14.7	1.17
0.074	0.014	0.926	0.986	5.2	0.72
0.094	0.024	0.906	0.976	4.1	0.61
0.141	0.031	0.859	0.969	5.2	0.72
0.275	0.062	0.725	0.938	6.9	0.84
0.349	0.106	0.651	0.894	5.9	0.77
0.462	0.180	0.538	0.820	5.8	0.76
0.545	0.266	0.455	0.734	5.4	0.73
0.603	0.409	0.397	0.591	3.4	0.53
0.824	0.711	0.175	0.288	3.3	0.52

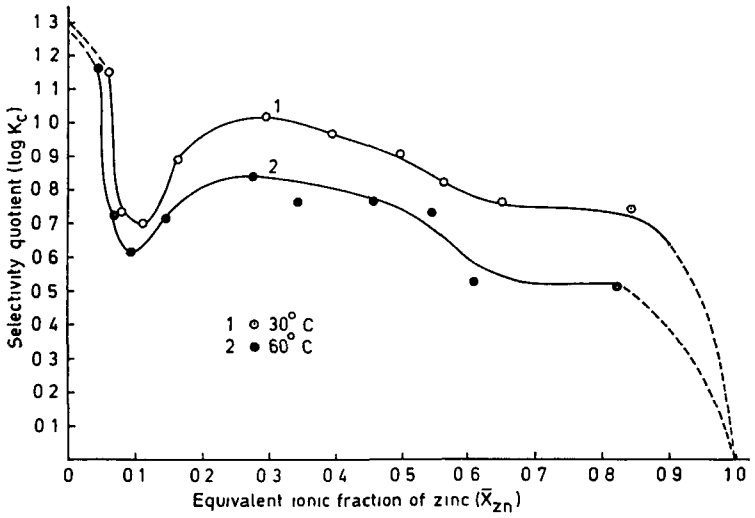

Fig 4 Zinc sodium selectivity in montmorillonite

coefficients is represented *vide* Fig 4 During the exchange, the selectivity quotient initially decreased, followed by a rise and then a fall at both the temperatures Such a variation was indicative of significant interactions between Zn and Na-montmorillonite, the preference of Zn for the solid surface varying according to the nature of the curves (Fig 4)

For a further examination of the equilibria, the thermodynamic equilibrium constant K was calculated from the simplified relationship of GAINES and THOMAS (1953)

$$\ln K=(Z_B-Z_A)+\int_0^1 \ln K_C \, d\,\bar{X}_{Zn}\,, \qquad (4)$$

where Z_A was the valence of Na and Z_B of Zn For the derivation of the above simplified formula from GAINES original relationship it became necessary to assume that $\oint_B^{Z_A}(b)=\oint_A^{Z_B}(a)$, namely that the activity of water was constant That this was so was borne out by the fact that the equilibria was carried out in dilute suspensions with a constant volume of water in the mixture

The values of K were obtained by evaluating the integral from the areas under the curves (Fig 4) using the trapezoidal rule The values are given in Table 2 A higher value of K at 30 than at 60°C indicated a higher preference of Zn for the clay at the lower temperature Further Zn was preferred over Na by montmorillonite

The standard free energy of exchange, ΔG^0 was calculated from the equation

$$\Delta G^0 = -RT \ln K\,, \qquad (5)$$

Table 2. Thermodynamic values of the Zn exchange on Na- montmorillonite at 30 and 60°C.

Thermodynamic parameters	30°C	60°C
K	18.0	11.9
ΔG^0 (cal/mole)	−1742	−1628
ΔH^0 (cal/mole)	−2744	
ΔS^0 (cal/mole)	−3.3	−3.3

and the standard enthalpy change ΔH^0 from van't Hoff isochore,

$$\ln \frac{K_{T_2}}{K_{T_1}} = \frac{-\Delta H^0}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right). \tag{6}$$

The standard entropy change, ΔS^0 was then obtained by the equation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 . \tag{7}$$

The values are listed in Table 2.

During the exchange of Na with Zn over montmorillonite the free energy change was negative over both the temperatures, that at 30°C being still more negative than the one at 60°C. At both the temperatures the exchanges were, therefore, spontaneous, the order of preference being Zn > Na. The order of preference varied with temperature, being higher at 30 than at 60°C. The results were in accordance with the earlier inferences.

Negative enthalpy change (Table 2) indicated that the reaction was exothermic, or in other words the binding energy of 1 atom of Zn was lower than that of 2 atoms of Na. Thus Zn was more tightly bound to montmorillonite than Na. This was in accordance with the values of K_C being higher than unity (Table 1). The exchange was also ruled by entropy effects. The entropy loss was indicative of a greater order produced in the forward reaction during Zn transfer to montmorillonite. Entropy change included two reactions which occurred in the interface and the solution. In going from solution to solid phase some of the water of hydration of Zn ions was removed to give a more orderly structure of Zn ions on the surface with resultant immobilization and reduction in the degrees of freedom of Zn ions on the clay surface. This contributed towards entropy loss. Further the passage of Na ions from solid to water resulted in their enhanced hydration with greater ordering of water and a further entropy loss. There is evidence to support these facts (GAST and KLOBE, 1971; BIGGAR and CHEUNG, 1973).

The surface phase activity coefficients of sodium and zinc ions were calculated from the following expressions (MARINSKY, 1966):

$$\ln f_{Na} = \bar{X}_{Zn} \ln K_C - \int_0^{\bar{X}_{Zn}} \ln K_C \, d\bar{X}_{Zn} , \tag{8}$$

Table 3. The surface phase activity coefficients, excess free energies, enthalpies and entropies of mixing ΔG_m^x, ΔH_m^x, ΔS_m^x for Na-Zn exchange on montmorillonite at 30 and 60°C.

$\bar{X}_{Zn}$	f_{Na}	f_{Zn}	ΔG_m^x	ΔH_m^x	ΔS_m^x
			(30°C)		
0.058	1.01	0.01	−53.7	−222	−0.56
0.075	0.95	0.04	−177.1	−330	−0.51
0.107	0.94	0.05	−230.8	−402	−0.57
0.166	0.99	0.04	−325.7	−511	−1.61
0.299	1.06	0.06	−497.1	−937	−1.45
0.395	1.12	0.09	−545.2	−710	−0.55
0.499	1.07	0.14	−564.9	−882	−1.05
0.562	0.98	0.20	−556.3	−1117	−1.85
0.650	0.82	0.31	−504.3	−803	−0.99
0.843	0.89	0.54	−321.1	−959	−2.11
			(60°C)		
0.060	1.03	0.02	−136.3	−274	−0.41
0.074	0.97	0.06	−156.8	−396	−0.72
0.094	0.95	0.08	−188.1	−437	−0.75
0.141	0.98	0.07	−258.3	−500	−0.73
0.275	1.08	0.09	−405.0	−1052	−1.94
0.349	1.03	0.13	−458.9	−680	−0.66
0.462	1.01	0.20	−489.9	−906	−1.25
0.545	0.96	0.28	−475.8	−1304	−2.48
0.603	0.75	0.39	−448.3	−854	−1.22
0.824	0.74	0.68	−246.7	−1102	−2.52

and

$$\ln f_{Zn} = (\bar{X}_{Zn} - 1) \ln K_C - \int_{\bar{X}_{Zn}}^{1} \ln K_C \, d\bar{X}_{Zn} \,. \tag{9}$$

The values are given in Table 3. The values were indicative of a nonideal system resulting in an increase in heterogeneity in the distribution of Na ions and a decrease in heterogeneity in case of Zn ions on the solid surface. The results found support from the work of DEIST and TALIBUDEEN (1967) on ion exchange in soils.

To further examine the deviation of the heterogeneous system from ideality, the excess thermodynamic functions for the system were calculated from the following expressions (VANSANT and UYTTERHOEVEN, 1972, GAST and KLOBE, 1971):

$$\Delta G_m^x = RT \, (\bar{X}_{Zn} \ln f_{Zn} + \bar{X}_{Na} \ln f_{Na}) \,, \tag{10}$$

$$\Delta H_m^x = -RT^2 \left[X_{Zn} \frac{\partial \ln f_{Zn}}{\partial T} + X_{Na} \frac{\partial \ln f_{Na}}{\partial T} \right] , \tag{11}$$

and

$$\Delta G_m^x = \Delta H_m^x - T\Delta S_m^x \qquad (12)$$

The values are given in Table 3 The values of ΔG_m^x were negative at both the temperatures which meant that with respect to the pure forms the heterogeneous surface phases were more stable than they would be if the mixing were ideal, *i e*, the deviation from ideality occurred in the sense of a more stable mixture Negative enthalpies of mixing pointed to a more tightly bound mixture of Na and Zn ions The negative entropies of mixing were a pointer to a nonideal state of the mixture and a significant heterogeneity at the surface The difference in the hydration rates of the ions in the mixture resulted in a decrease in entropy with respect to the homo-ionic forms

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Adsorption of nicotine on dickite

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A study of the adsorption of simple organic molecules plays an important part in understanding the mechanism of their interactions with soil clays. Adsorption of organic compounds on clay surfaces depends upon several factors [10], [15] such as strong cation dipole attractions [3], hydrogen bonding [6], solvation of cations by polar molecules, coordination [13], cation exchange reactions, van der Waals interactions [6], pH and other environmental conditions.

Clay minerals constitute the most important reactive surfaces of the soil. They have been reported to provide heterogeneous chemical spots in the form of sorbed water around cations [18], hydroxyls at the edges, lattice surface oxygens and electrical double layer of changing polarity [14] at the edges. They possess electron accepting sites in form of exposed aluminium [17] and transition metals in higher valency state at the edges. The location [2] and distribution of exchange sites on clays is an important factor in the nature and extent of adsorption.

The mineral dickite, a polymorph of $Al_4(Si_4O_{10})(OH)_8$, has a structure somewhat similar to kaolinite. It is believed to carry Lewis and Bronsted acidic sites on its edge crystal faces [9]. FORDHAM [4] has demonstrated the existence of positive and negative sites at the edges of dickites along with some basal surfaces. The behaviour of such clay minerals, both chemically and physically depends to a great extent upon their surface energetics.

Nicotine is a polar heterocyclic compound. It is an electron donor in which the aliphatic nitrogen of the pyrrolidine ring is the donor species. It is an important pesticide. Its importance in the functions of the central nervous system is well known. A study of the adsorption and interaction of pesticides is of great importance because processes such as effective pesticidal action, their mobility, persistence and toxicity [11] in soils depend to a great extent upon the nature and interaction of the chemical with the silicate clays [16].

Adsorption isotherms and titration curves can be used to provide information on the mechanism of interaction of organics with

soils. Regular and discontinuous isotherms [19]) due to heterogeneities on the adsorbant surface have been observed. GILES *et al.* [5]), have classified the various shapes of adsorption isotherms with respect to the reaction mechanism concerned.

The primary objective of this work was to investigate the mechanism of adsorption and interaction of nicotine, a typical alkaloid on dickite, a void filling mineral of the algal limestones in its acid and base saturated forms in dilute clay water suspensions.

MATERIALS AND METHODS. — The dickite used in these studies was a monomineralic A.P.I. sample No 15 from Mexico obtained from Wards Natural Science Establishment Inc., Rochester, New York. It was dispersed in a mortar by grinding it lightly with a pestle and distilled water. The less than 2 u fraction obtained by repeated dispersion and centrifugation was converted into Na-clay by saturating it with molar NaCl several times. It was then washed with distilled water till no chloride was detected with $AgNO_3$ and till the conductivity of the suspension became constant. Hydrogen saturated dickite was prepared just prior to the required experiments, as per Aldrich and Buchanan's[1]) method, by ion exchange technique. The concentration of the suspensions varied from 2,0 to 9,0 g. of clay per litre of suspension.

The H-dickite samples were subjected to potentiometric and conductometric titrations with nicotine as well as with NaOH. The results are given vide Figs. 1-2.

Adsorption experiments were conducted with temperature around 30°C by taking 10 ml of the appropriate clay suspension in a number of glass stoppered tubes, and adding various amounts of nicotine solution (0,5 g per litre), and deionised water to obtain a fixed final volume. After intermittent shaking and standing for 72 hours the suspensions were centrifuged, their pH and electrical conductivity recorded and the residual nicotine estimated with standard HCl. The amount of absorbed nicotine was determined as the difference between the amounts of nicotine added and remainig. Adsorption isotherms were plotted between equilibrium concentration and mmoles of nicotine adsorbed per 100 g. clay (Fig. 3).

The adsorption data was examined with the help of X-ray diffraction. The X-ray analysis was done on acid and base saturated samples of $<$ 2 u dickite, on samples treated with nicotine and glycerine. For X-ray analysis the samples were oriented on glass microslides from a water suspension at room temperature. They were then air dried, solvated with glycerol and heated at 550°C for 2 hours. Patterns were obtained using filtered Cu K radiation on a « Mikrometa » goniometer at a speed of 2° per minute. Basal spacings in A° deduced from the positions of 001 reflections are given in table II.

RESULTS AND DISCUSSION. — The results of potentiometric and conductometric titrations of H-dickite with NaOH and nicotine are given vide table 1, figures 1-2. The figures (curves 3 and

4) also show the changes that occurred in the pH and conductance during adsorption of nicotine by acid and base saturated dickites. The figures in parentheses in the table indicate the pH at the inflection points. The meq. of base per 100 g. clay as obtained from the inflections gave the base exchange capacities.

Adsorption of nicotine on acid and base saturated dickites in dilute suspensions in the equilibrium concentration range of 0.0 to 1.0 mmole of nicotine per litre yielded isotherms vide Fig. 3. An examination of the isotherms revealed that the isotherm for hydrogen saturated dickite was similar to class ' H ' isotherm as defined by GILES *et al.* [5]), and that for the sodium saturated system

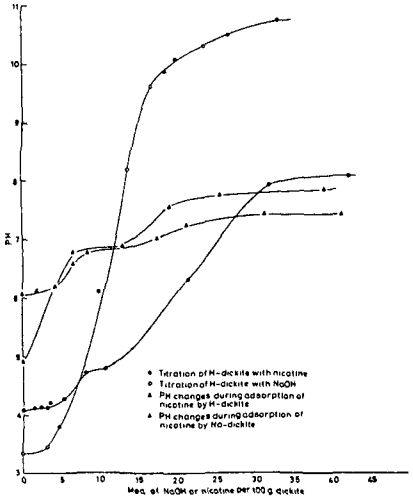


FIG. 1. — Potentiometric titration of dickite with nicotine and NaOH and changes during adsorption.

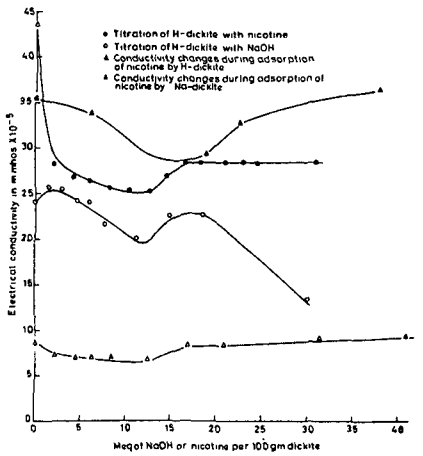


FIG. 2. — Conductometric titration of dickite with nicotine and NaOH.

TABLE 1. — *Main inflections and base exchange capacities of acid and base saturated dickites as obtained during titration and adsorption.*

Mineral form	Nicotine as titrant and absorbate				Sodium hydroxide as titrant	
	Point titration		Changes during adsorption			
	Potentiometry	Conductometry	Potentiometry	Conductometry	Potentiometry	Conductometry
H-dickite	15.0(5.2)	12.5	15.0 (7.1)	15.0	14.0 (8.5)	12.5
Na-dickite	—	—	15.0 (6.9)	12 5	—	—

TABLE 2 — *Basal spacings of H, Na, nicotine, glycerine and heated treated samples of dickite*

Nature of dickite	Basal spacings at 001 reflections in A°	Interlamellar separation in A°
H-saturated dickite	7.07 (S)	—
Nicotine treated H-dickite	7 13 (W)	0.06
Na-saturated dickite	7.05 (S)	—
Nicotine treated Na-dickite	7.00 (M)	Nil
Nicotine complex treated with glycerine	7 00 (W)	Nil
Na-saturated dickite at 550° C	Collapsed	—
Nicotine complex at 550° C	Collapsed	—

Letters in parenthesis in column II indicate intensities
S = strong, M = medium and W = weak.

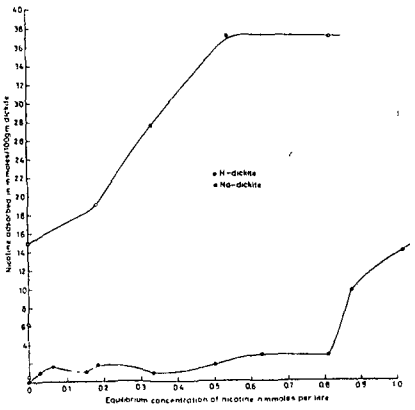
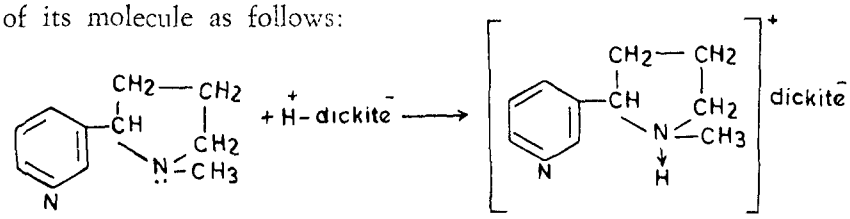
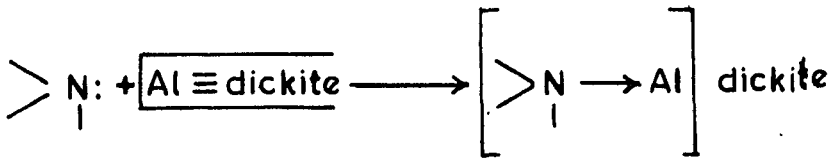


FIG. 3. — Adsorption isotherms of acid and base saturated dickites.

similar to class ' L '. The adsorption in the two cases was thus very much different. The initial part in the case of the isotherm for the acid H-dickite was vertical indicating that nicotine had such a high affinity for the acid dickite that in dilute suspensions it was completely adsorbed till a limiting value (15.80 mmoles) was reached at a point corresponding to complete saturation of its base exchange capacity and a pH = 7.10. An inflection or «knee» occurred at this point indicating completion of the first degree saturation. Such an initial steep rise was indicative of chemisorption with edge to edge ion attraction [7]). An increase in pH (Fig. 1, curve 3) and a decrease in electrical conductance (Fig. 2, curve 3) with an inflection similar to that obtained during titrations pointed to removal of protons during the interaction. The initial adsorption of nicotine on H-dickite, therefore, appeared to be due to the donation of electrons by nicotine to H-dickite resulting in coordination of its molecule as follows:



The subsequent rise in adsorption beyond the inflection (Fig. 3, curve 1) pointed to an interaction of nicotine with the Bronsted [8]) or Lewis acid [17]) sites at the crystal edges of dickite. It has, however, been reported that Bronsted acid sites at the crystal edges of clays are not strong [12]) enough to react with weak bases like pyridine. Hence in the case case of nicotine the Lewis acid character of dickite edges appeared to predominate. With aluminium at the edges thus acting as an electron acceptor and nicotine as an electron donor, a subsequent interaction resulted as follows:



With the saturation of these sites the adsorption of nicotine in acid dickite became constant (Fig. 3, curve 1). This found support from the pH and conductance change which also became nearly constant (Figs. 1-2, curves 3) at this stage.

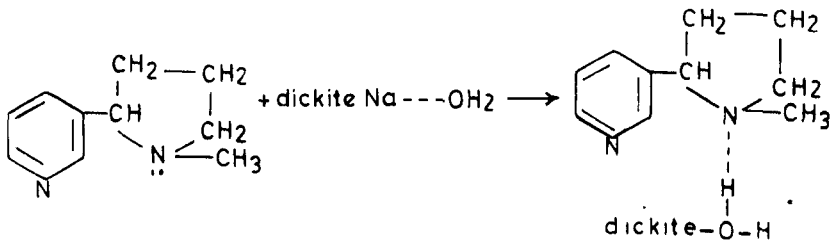
Inspite of the greater deflocculation effect and larger surface area exposed by Na-dickite in comparison to H-dickite, a very small amount of nicotine was initially adsorbed by the sodium saturated dickite. This happened till an equilibrium concentration of 0.8 mmoles of nicotine was reached. As is often observed in cases of 'L' curves it thus appeared that nicotine molecules had some difficulty in finding vacant sites on the surface of Na-dickite. Fluctuations in the small adsorption were also observed in the earlier stages of the interaction suggesting changes from hydrophobic to hydrophilic nature in the clay system.

The nature of exchangeable cation in dickite thus seemed to determine the extent of adsorption. The order of adsorption found confirmation from the partial molar free energy changes that occurred during the interaction. The changes in partial molar free energy F were calculated from the thermodynamic relationship

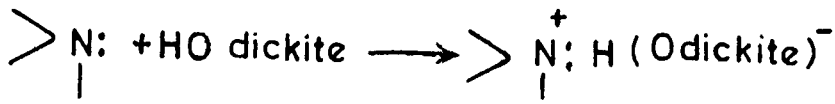
$$-\bar{F} = RT \ln \frac{C_e}{C_o}$$ where C_e and C_o were the equilibrium and initial concentration of the suspension respectively. An average of five values of $\bar{F}$ in case of H- and Na- saturated dickites yielded 301.0 and 204.3 cal/mol respectively, thus confirming the extent

of the driving force available for the adsorption of nicotine on the dickites.

The small amount of nicotine adsorbed in the earlier concentration range by Na-dickite and its marked difference from that observed in acid clay suggested that nicotine was adsorbed in this range through comparatively weak adsorptive forces at a binding site different from that in the case of the acid system. The interaction of nicotine with Na- dickite can be ascribed to formation of coordination bonds, capacity of nicotine to desorb water from around Na^+ ions giving rise to proton transfers, hydrogen bonding with directly coordinated water and interaction with the weakly acidic sites at the edges. Possibility of coordination of nicotine to Na^+ ions or proton transfers from adsorbed water would result in significant conductivity changes which were not observed in the present case. The small amount of adsorption of nicotine on Na-dickite in the early stages, therefore, appeared to be due to formation of hydrogen bonds between the pyrrolidine nitrogen of nicotine and the coordinated water as follows:



With the saturation of the above sites and crossing of the energy barrier, the electron acceptor Al or the weakly acidic hydroxyls at the edges of dickite took over and a sudden jump in chemisorption occurred vide equation (2), as in the case of acidic dickite (Fig. 3, curve 2), or vide equation (4) as follows:



There is evidence that clay surfaces even when saturated with basic cations act as weak to moderately weak acids [18]).

Examination of the nicotine- dickite complexes under X-ray diffraction did not yield any marked increase in basal spacing (Table 2). Treatment of the complex with glycerine showed no variation. Heat treatment at 550°C resulted in a complete collapse of the dickite peaks. These observations were in line with the fact that no lateral surface was available in dickite for the interaction with nicotine and only the edge sites took part in the interaction

ACKNOWLEDGEMENT — Thanks are due to Prof Mohsin Qureshi for providing laboratory facilities

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SUMMARY. — The adsorption of nicotine on acid and base saturated dickites yielded cation dependent adsorption isotherms similar to class « H » and « L » respectively. The pH, electrical conductivity changes and adsorption pointed to initial coordination of the nicotine molecule with H-dickite followed by interaction with the « Lewis » acid sites at the edges. Adsorption of nicotine on Na-dickite, on the other hand, was weak and manly due to hydrogen bonding followed by chemisorption at the edges. X-ray diffraction provided evidence that only edge sites were involved in the reaction.

RÉSUMÉ. — Par l'adsorption de nicotine sur un acide ou une base saturée, on a obtenu d'isotherms d'adsorption, qui dépendent des cations et qui ressemblent à la classe « H » ou « L » respectivement. Les changements de pH, de conductivité et d'adsorption indiquent une coordination initiale entre les molécules de nicotine « Lewis » aux bords. L'adsorption de nicotine sur dickite de Na était, par revanche, faible et principalement à cause de bondage hydrogénique suivant la chemisorption aux bords. La diffraction des rayons-X a mis en évidence le fait que seulement les bords s'impliquent à l'interaction.

ZUSAMMENFASSUNG. — Die adsorption des Nikotins an säure und base Dickites gab, (wie bei Klassen «H» und «L») Kation abhängige adsorptions génique suivant la chemisorption aux bords. La diffraction des rayons-X a mi isotherme. Das pH, elektriche leitfahigkeit veranderungen und adsorption, wiesen auf eine primare adsorption des Nikotin moleküles an H-Dickite und nachfolgende Reaktion mit Lewis Saure Stellen an die Kanten. Nikotin adsorption an Na-Dickite war dagegen schwach und hauptsachlich durch, H-bindungen, zusammen mit chemisorption an die Kanten, Dass hierbei nur die Randstellen eine rolle spielten wurde Rontgenographich bewiesen.

RESUMEN. — La absorción de la nicotina en el ácido y la base de dickites saturada produjo isotermas de absorción dependiente de cation semejantes a las clases « H » y « L » respectivamente. Los cambios de conductibilidad eléctrica pH y la absorción senalarón una coordinación inicial de las moléculas de la nicotina con la H-dickite seguida de una interacción con los sitios de ácido Lewis en los bordes. La absorción de la nicotina en la Na-dickite, por otro lado, era poca, debido, sobre todo, del vénculo del hidrógeno, sequido de chemisorption en los bordes. La difracción de los X-ray dio evidencia de que sólo los lugares de los bordes tomarous parte en la reacción.

RIASSUNTO. — L'assorbimento della nicotina su acido e base saturate dei dickiti fornisce Catione dipendente da assorbimento di isotermi simili alla classe « H » e « L » rispettivamente. I cambiamenti di PH, di conducibilità e di assorbimento indicano una coordinazione iniziale della molecola della nicotina con H-dickite seguito dalla interazione con le posizioni dell'acido «Lewis» sui margini. L'assorbimento della nicotina su Na-dickite, d'altra parte, era debole principalmente a causa della lega dell'idrogeno seguito dall'assorbimento chimico ai margini. La diffrazione a raggi-X evidenzia che soltanto le posizioni ai margini erano implicate nella reazione.

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THERMODYNAMICS OF THE EXCHANGE OF NICOTINE ON ALUMINIUM-MONTMORILLONITE

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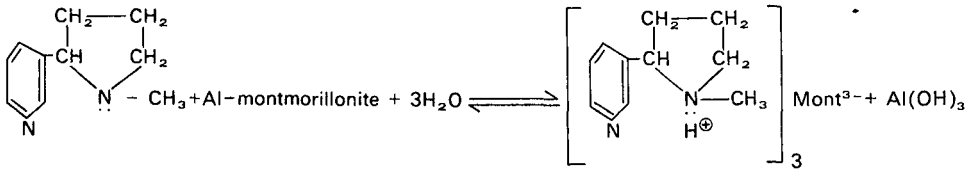
Summary

The ion exchange equilibria involving the interaction of nicotine with Al-montmorillonite was studied thermodynamically. The exchange isotherms at 30° and 60 °C indicated a preference for Al ions by montmorillonite as compared with nicotinium ions. A separation factor supported the conclusion. The enthalpy gain indicated tighter binding of Al. The entropy gain indicated a diffused and disordered arrangement of nicotinium ions in the Goüy layer with Al forming a more ordered arrangement in the Stern layer.

Introduction

A STUDY of the adsorption of pesticide molecules plays an important part in understanding the mechanism of their interaction with soil clays. Nicotine is a cationic molecule in which the aliphatic nitrogen of the pyrrolidine ring is the electron-donor species.

Clays constitute the most important reactive surfaces of the soil. They provide sites for cation exchange and many other reactions and form clay-organic complexes. In its aluminium-saturated form montmorillonite behaves as a Brönsted acid (Lloyd and Conley, 1970) to supply protons to nicotine in aqueous medium, as has been shown for many amines. With nicotine it can undergo the following exchange reactions



Investigations in these laboratories revealed that the above reaction was reversible (Singhal and Singh, 1970).

The importance of a study of the retention of complex pesticides such as nicotine on acid soils led us to investigate the action of nicotine on Al-montmorillonite with the help of exchange isotherms and thermodynamic parameters. The treatment is mostly based on the thermodynamic treatment of previous workers (Gaines and Thomas, 1953; Howery and Thomas, 1965; Singhal and Singh, 1973).

Experimental

The clay was montmorillonite from Polkville, Mississippi, with a cation exchange capacity of 90 me/100 g clay as determined by the ammonium acetate method. It was dispersed, and the $< 2\ \mu m$ clay was separated by

centrifugation and converted into Na-montmorillonite by treatment with 2M NaCl. Al-montmorillonite suspension was prepared from the Na-clay by saturating it repeatedly with 0·33M $AlCl_3$ at pH 3·2 and washing with deionized water to remove the excess salt. The pH of the resultant suspension was 5·1. Treatment of the Na-clay with $AlCl_3$ resulted in a reduction of the CEC. The CEC of the Al-montmorillonite, determined by extraction of the Al-saturated suspension with a solution of 0·1M HCl in 1M NaCl (Frink and Peech, 1963) was 70 me/100 g montmorillonite.

The concentration of Al-montmorillonite suspension was 8·5 g per litre. It showed an ageing effect for the first 24 h, shown by a slight increase of aluminium in the supernatant liquid. During the next 12 h the concentration of soluble aluminium was constant. The exchange experiments were conducted during this period to avoid any significant effects of ageing.

The exchange isotherms were determined by placing 10 ml samples of Al-montmorillonite in a number of glass-stoppered tubes. Various amounts of 0·03077M nicotine were added and the volume was made up to 25 ml with distilled water. The tubes were shaken for 12 h at 30±0·1 °C in the first set of experiments and 60±0·1 °C in the second set to attain equilibrium. The mixtures were centrifuged and aluminium and nicotine estimated in the supernatant liquids. Aluminium was estimated colorimetrically using aluminon (Jackson, 1958) as colour reagent, and nicotine with standard HCl using methyl red as indicator. The corresponding concentration of aluminium in the clay phase was obtained by difference (Al-CEC minus concentration of the cation in the supernatant liquid) and that for nicotine from nicotine added minus the nicotine in the supernatant liquid.

Results and discussion

The exchange reaction between nicotine and Al-montmorillonite in dilute suspensions can be described by the equation:

$$\bar{C}_{Al}+C_{nicotine} \rightleftharpoons C_{Al}+\bar{C}_{nicotine}. \qquad (1)$$

The barred quantities refer to the equivalent concentrations of each ion in the clay phase, and the unbarred to the concentrations in the solution. The equivalent ionic fractions (X) of nicotine and aluminium in montmorillonite and in solution were calculated from the expressions

$$\bar{X}_{nicotine}=\frac{\bar{C}_{nicotine}}{\bar{C}}, \qquad X_{nicotine}=\frac{C_{nicotine}}{C},$$

$\bar{X}_{Al}=\bar{C}_{Al}/\bar{C}$ and $X_{Al}=C_{Al}/C$, where $\bar{C}$ and C were the total amounts of aluminium and nicotine in the clay and solution phases respectively.

The values obtained both at 30° and 60 °C are shown in Fig. 1. The deviation of the isotherms from the diagonal indicated a strong preference by montmorillonite for aluminium as compared with nicotine at both the temperatures over the entire range of concentration studied.

The affinity of montmorillonite for nicotine was further examined by the separation factor:

$$\alpha_{Al}^{nicotine} = \frac{\bar{X}_{nicotine}}{\bar{X}_{Al}} \cdot \frac{X_{Al}}{X_{nicotine}}. \qquad (2)$$

Values lower than unity (Table 1) at both temperatures indicated a higher preference by montmorillonite for trivalent Al than for the

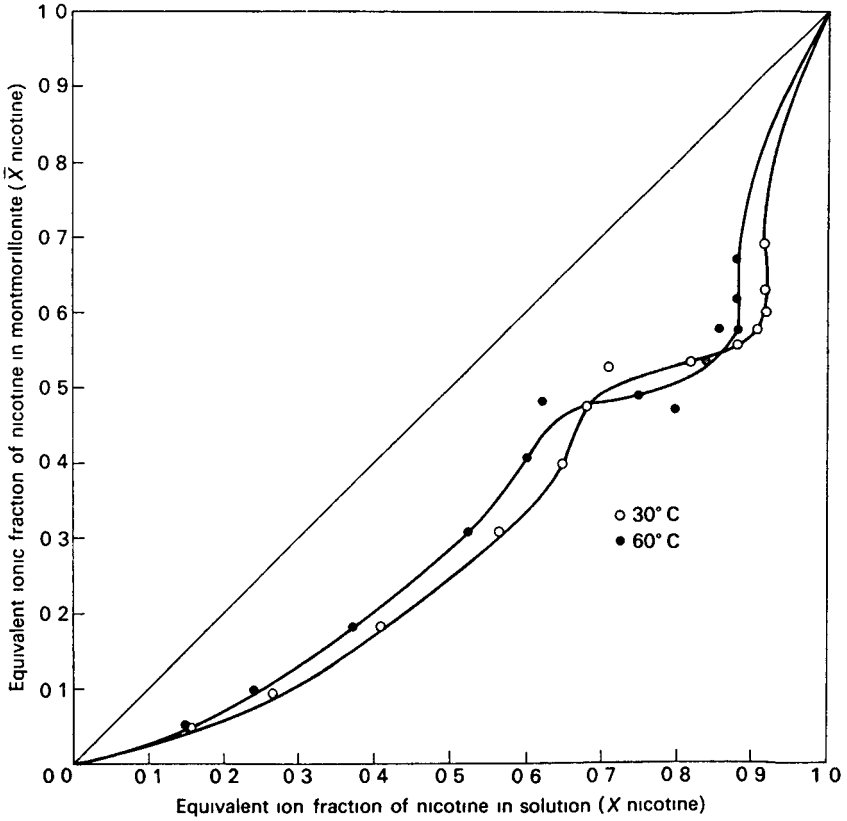


FIG. 1. Exchange isotherms of nicotine on Al-montmorillonite at different temperatures.

organic ion. However, the preference for nicotine as indicated by the separation factor increased with an increase in its concentration to a certain concentration of nicotine ($X_{nicotine}$) after which it declined. The separation factor was also larger at the higher temperature (Table 1) indicating an increase in the preference for nicotine with rise in temperature.

Taking the ratio of activity coefficients as unity (Robinson and Stokes, 1959) in the dilute range of concentration studied, the selectivity

TABLE I

Values of equivalent ionic fractions of aluminium and nicotine and selectivity quotients at 30° and 60 °C for the nicotine exchange with Al-montmorillonite

Sl. No.	$\bar{X}_{Al}$	X_{Al}	$\bar{X}_{nicotine}$	$X_{nicotine}$	$\alpha_{Al}^{nicotine}$	K_c	Log K_c
				30 °C			
1.	0·948	0·843	0·052	0·156	0·296	0·0234	−1·631
2.	0·901	0·735	0·099	0·265	0·305	0·0438	−1·460
3.	0·819	0·590	0·181	0·410	0·318	0·0616	−1·210
4.	0·692	0·435	0·307	0·565	0·342	0·1007	−0·997
5.	0·599	0·353	0·401	0·647	0·365	0·1403	−0·853
6.	0·525	0·317	0·475	0·683	0·420	0·2031	−0·692
7.	0·467	0·286	0·533	0·713	0·458	0·2557	−0·592
8.	0·465	0·178	0·535	0·822	0·249	0·1055	−0·977
9.	0·437	0·121	0·563	0·879	0·177	0·0727	−1·139
10.	0·423	0·090	0·577	0·909	0·135	0·0544	−1·264
11.	0·399	0·078	0·601	0·922	0·127	0·0541	−1·267
12.	0·370	0·079	0·630	0·921	0·146	0·0683	−1·166
13.	0·309	0·083	0·690	0·917	0·202	0·1144	−0·942
				60 °C			
1.	0·947	0·850	0·052	0·150	0·311	0·0263	−1·580
2.	0·900	0·759	0·100	0·241	0·349	0·0602	−1·220
3.	0·817	0·631	0·187	0·369	0·391	0·1000	−1·000
4.	0·689	0·480	0·311	0·520	0·417	0·1491	−0·827
5.	0·594	0·402	0·406	0·598	0·459	0·2119	−0·674
6.	0·516	0·382	0·484	0·618	0·580	0·3557	−0·449
7.	0·508	0·252	0·492	0·748	0·362	0·1411	−0·851
8.	0·527	0·199	0·473	0·801	0·223	0·0777	−1·110
9.	0·458	0·164	0·542	0·836	0·232	0·0975	−1·011
10.	0·420	0·144	0·580	0·855	0·233	0·1070	−0·971
11.	0·423	0·120	0·577	0·880	0·186	0·0799	−1·098
12.	0·381	0·119	0·619	0·881	0·219	0·1083	−0·965
13.	0·326	0·117	0·674	0·883	0·274	0·1596	−0·797

coefficients at various values of $\bar{X}_{nicotine}$ were calculated from the expression (Reichenberg, 1966):

$$K_c = \frac{\bar{X}_{(nicotine)}^3 (X_{Al})}{(\bar{X}_{Al})(X_{nicotine})^3}. \quad (3)$$

A plot of the values of K_c at 30° and 60 °C is given in Fig. 2.

For a further study of the affinity, the thermodynamic equilibrium constant K was calculated from the relationship:

$$\ln K_c = (Z_A - Z_B) + \int_0^1 \ln K_c \, d\bar{X}_{nicotine} \quad (4)$$

where Z_A and Z_B were the charges on the competing ions. The integral was evaluated from the areas under the curves (Fig. 2) using the trapezoidal rule. The value of K at 30 °C was lower than at 60 °C

indicating that nicotine had a higher preference for montmorillonite at the higher temperature (Vansant and Uytterhoeven, 1972).

The Gibbs free energy for the interaction was obtained by the equation:

$$\Delta G^\circ = -RT \ln K. \tag{5}$$

The negative value of free energy implied a higher preference for nicotine. That was, however, not conclusive because formation of

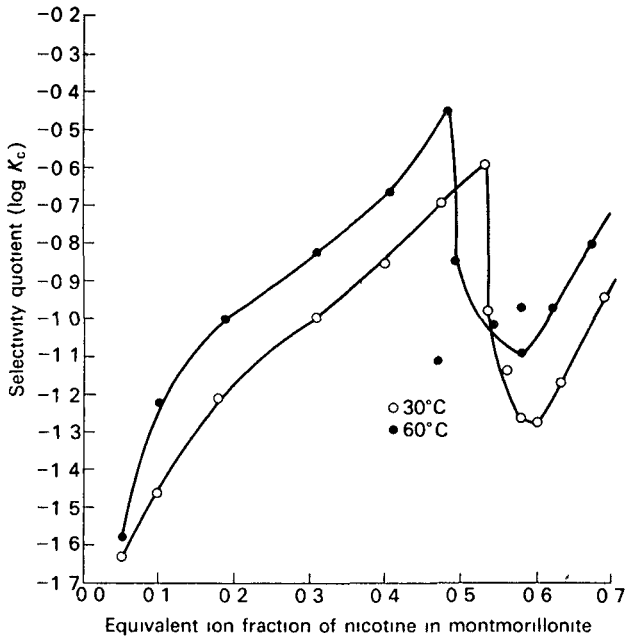


FIG. 2. Logarithms of selectivity quotients vs. equivalent ionic fraction of nicotine in montmorillonite.

nicotinium clay was accompanied by an increase in enthalpy pointing to a stronger binding of Al.

The standard enthalpy change was calculated from the Van't Hoff isochore:

$$\ln\left(\frac{K_{T_2}}{K_{T_1}}\right) = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right), \tag{6}$$

and the standard entropy change by the equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ.$$

The values given in Table 2 indicate that the interaction was affected both by enthalpy and entropy effects. The positive value of enthalpy suggested temperature-dependent adsorption and that nicotine was less strongly bound on the montmorillonite surface than aluminium. Entropy gain accompanying nicotine adsorption further justified this assumption. It indicated a more diffuse and disordered arrangement

TABLE 2

Thermodynamic values for the nicotine exchange with aluminium montmorillonite at 30° and 60 °C

Thermodynamic parameters	*Values at 30 °C*	*Values at 60 °C*
K	1·51	1·90
ΔG° Cal/moles	−247	−424
ΔH° Cal/moles	1539	
ΔS° Cal/moles	5·89	5·89

of nicotinium ions in the Goüy layer with aluminium forming a more ordered arrangement in the Stern layer. Valence, electrostatic considerations, and the smaller size of Al ions as compared with the nicotinium ions justified the conclusion.

Acknowledgement

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Effect of D-D Mixture on Availability of Some Plant Nutrients in a Black Cotton Soil

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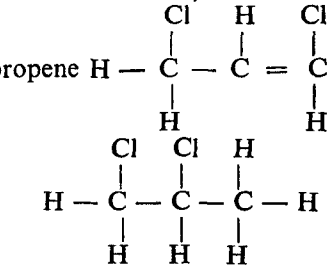
Abstract : *The effects of D-D mixture, on major nutrient availability of a black cotton soil were examined. The results showed that while in smaller doses the fumigant significantly stimulated the availability of N and P, higher doses tended to be toxic. Lower doses had a non-significant suppressive influence on K availability. Organic matter was significantly reduced with increasing doses of D-D mixture. In general the stimulation after reaching a maximum gradually declined. The results have been explained on the basis of microbial activity.* (Key words : D-D mixture ; soil properties ; black cotton soil).

Carbon disulphide, ethylene dibromide, methyl bromide, nemagon and telone have been extensively tried for the control of nematodes, fungi and other microbial pests (Minz & Palti 1954; Taylor 1951). The interaction of the fumigants with soil ingredients have been useful as well as inhibitory (Hanson & Nex 1953) to plant nutrients. The cumulative effects of adsorption, persistence and degradation of the nematocides in soil may result in toxic (Newhall 1951) and pollution hazards. The present work was undertaken with a view to examine the effects of a mixture (50: 50) of 1,3 dichloropropene and 1,2 dichloropropane on organic matter and N,P,K of a black cotton soil.

EXPERIMENTAL

A black cotton soil sample (depth 0-30 cm) was collected from Kota district (Rajasthan, India). It was dried, crushed and sieved through 4 mm sieve. The general characteristics of the soil were : pH = 8.05, E.C. = 6.3×10^{-4} mhos/cm, available N = 0.0056%; available P = 0.0012%; available K = 0.0075%; org. matter = 0.68% and $CaCO_3$ = 3.5%.

The fumigant used was D-D, a mixture of 1,3 dichloropropene and 1,2 dichloropropane



(50 : 50) with traces of other hydrocarbons. The chemical was obtained from M/s Burmah Shell (NOCIL), New Delhi.

The experiments were conducted in earthenware pots of 25 × 25 cm size which were coated with coaltar to prevent adsorption of water. Two kg of the soil was taken in each of the 18 pots. Zero day samples were drawn from the pots. The soil was then saturated to 25% by weight with distilled water. Six doses of D-D mixture (0.00, 0.25, 0.50, 0.75, 1 00 and 1.25 ml per kg soil) were injected at a depth of 15 cm in three replications without growing any crop. All the samples were watered with 150 ml distilled water per week throughout the period of experiment. Distilled water was used to avoid any contamination with impurities. Samples were periodically drawn from the pots at an interval of 15 days upto 90 days and the effects of the nematocide on N, P, K and organic matter examined.

Organic matter was estimated as per Walkley and Black (1947) method and available N as per alkaline $KMnO_4$ method (Subbiah & Asija 1956). Available P was determined colorimetrically by Olsen's (1954) method. Available K was estimated turbidimetrically (Datta *et al.* 1968) with Spectronic '20' at 660 mμ.

RESULTS AND DISCUSSION

The effects of D-D mixture on organic matter, available N, P and K in black cotton soil are recorded in table 1. Each datum in the table for individual doses represents a mean of seven values recorded 0, 15, 30, 45, 60, 75 and 90 days after application of the fumigant. Similarly the average values for different days represent a mean of several values obtained at different doses, *viz.*, @ 0.0, 0.25, 0.50, 0.75, 1.00, and 1.25 ml per kg soil. The data were subjected to statistical analysis of variance according to the two way classification and LSD values were calculated using the value of t at 5% level of significance. In the discussion that follows only the average values for doses and days have been considered and the term significant is used as meaning statistically significant at 5% F level (2.52 for doses and 2.42 for days).

Effect on Organic Matter

A reference to the data incorporated in table 1 show that as compared to the control, the amount of organic matter significantly decreased with increasing applications of the fumigant. With passage of time, however, it significantly increased, though still below the control, reached a maximum at 45 days and then significantly declined. The evidence for the decline in organic matter is provided by the fact that while fumigants like D-D greatly eliminate nematode population, many soil bacteria are fairly resistant to fumigants. The eradicant-type chemicals produce greater reinvasion potentials (Klemmer 1957) with the results that the reactivated soil organisms bring about a rapid decomposition of organic matter which significantly declines. Such effects have also been reported by Smith *et al.* (1947).

Effect on Available Nitrogen

Availability of N (Table 1) was found to significantly increase upto an application of 0.50 ml of the fumigant per kg of soil and upto 30 days. Thereafter a significant decline was observed in both cases.

The initial increase in available N was due to the decomposition of soil organic matter by fumigant resistant bacteria (Klemmer 1957) which resulted in the release of N. The decrease with large doses on the other hand appeared to be due to the inhibitory effects of large doses of the fumigant on nitrification (Koike 1961). The decline with passage of time was due to the dissipation of the toxic chemical and reinfestation of the high potential zones of the treated soil by the fast growing fungi of the vigorously competitive sugar and amino acid utilising kinds (Kreutzer 1965).

Effect on Available Phosphorus

A reference to table 1 revealed that the availability of P increased with application

TABLE 1

Effect of D-D mixture on nutrient availability for different doses of the mixture at various intervals of time

Treatment Doses (in ml per kg of soil) and duration (days)	Average values of available nutrients for various doses and days in mg per 100 g soil			
	Org. matter	N	P	K
0.00	730.4	12.78	1.49	12.35
0.25	729.6	13.27	1.50	11.86
0.50	718.5	13.37	1.60	11.40
0.75	714.5	13.31	1.67	11.27
1.00	709.8	12.68	1.52	11.91
1.25	703.0	12.62	1.46	12.09
LSD	10.4	0.53	0.08	0.54
Variance ratio	12.6	5.45	10.29	0.37
0 day	684.3	5.60	1.16	7.50
15 days	698.0	12.95	2.04	13.04
30 days	755.5	16.31	2.37	13.68
45 days	761.2	15.85	1.56	13.27
60 days	722.2	14.06	1.37	12.35
75 days	707.9	13.26	1.28	11.76
90 days	695.5	12.80	1.20	11.03
LSD	9.5	0 50	0.07	0.49
Variance ratio	82.4	412.40	242.02	191.42

of D-D mixture upto 0.75 ml/kg of soil and it reached a maximum value at 30 days. Higher doses and days reduced the availability. All the effects were statistically significant.

Several workers (Wensley 1953 ; Martin *et al.* 1957) have reported increased and highly stimulated microbial activity in soil as a result of fumigation. The action of ascomycetes, actinomycetes and the reinfested fungal flora resulted in the decomposition of soil organic matter bringing about a gradual increase in P availability till a peak was reached both with doses and time. However, the toxic effect of too high doses and certain chemical reactions like reduction of P to PH_3 with passage of time resulted in the decline of P. Further work is, however, needed to establish the latter point.

Effect on Available Potassium

The effect of D-D on K availability with increasing doses was non-significant (Table 1). The up and down trend with passage of time though statistically significant followed the trend in the control. At the most, therefore, it could be said that D-D had a slight suppressive influence on K availability in soil. The mechanism by which this occurred was not entirely clear. Probably

the fumigant had a tendency to fix available K into non-exchangeable form on the clay lattice but further work is required to justify this conclusion.

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The authors are grateful to Dr. Abrar Mustafa Khan, Professor of Botany, Aligarh Muslim University, for helpful suggestions.

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Effect of D-D Mixture on some Nutrients of a Saline Sodic Soil

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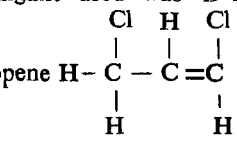
The effects of different doses of D-D mixture, a well known nematocide, on some characteristics of a sodic saline soil were examined. The results revealed significant favourable and toxic responses of the fumigant on N,P,K and organic matter of the soil with passage of time. There was no marked effect on the *p*H and electrical conductivity. The results have been explained on the basis of microbial activity.

PESTICIDES are widely used in agricultural production. They are used as insecticides, herbicides, fungicides and nematocides. Their use is attendent with varied physical, chemical and biological changes in soils.[1,2] Some work on the major nutrient availability in soils in presence of pesticides has been reported by Freney[3], Castro[4], Wedding et al.[5], Alexander[6], Thiegs[7] as well as Shanker and Kumar.[8] Their findings are, however, not entirely in agreement. Since the *p*H changes and nutrient availability have a profound influence on crop production, and since the use of pesticides in agriculture is increasing, it was thought worth-while to examine the effects of different concentrations at various intervals of time of an important nematocide viz., a 50:50 mixture of 1,3 dichloropropene and 1,2 dichloropropane on the nutrient availability (N,P,K and organic matter) in a widely occurring sodic saline soil. Effects on *p*H and EC are also recorded.

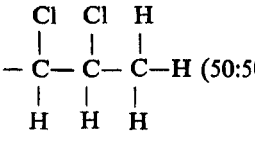
Experimental

The soil used in the study (depth 0-30 cm) was collected from a representative area of Aligarh district. It was dried, crushed and sieved through 4 mm sieve. The general characteristics of the soil were determined and yielded the following data : *p*H = 9.31, E.C. = 26.3 $\times 10^{-4}$ mhos/cm, available nitrogen 0.0028%, available phosphorous=0.0006%, available potassium=0.0053% and organic matter = 0.291%

The fumigant used was D-D, a mixture of 1,3 dichloro-propene



and 1,2 dichloro-propane



(50:50) with small amounts of other hydrocarbons.

The experiments were conducted in earthenware pots of 25 × 25 cm size. The pots were cleaned and coated with coaltar to prevent adsorption of water. Two kg of the soil was taken in each of the 18 pots. Zero day samples were then drawn from the pots. The soil was then saturated with 20% distilled water by weight. Six concentrations of D-D mixture (0.0, 0.5, 1.0, 1.5, 2.0 and 2.5 ml) were injected at a depth of 15 cm in three replications without growing any crop. All the samples were then watered with 100 ml distilled water per week throughout the period of experiments. Distilled water was used to avoid any contamination with impurities. Samples were drawn at an interval of 15 days upto 90 days and the effects of the nematocide on *p*H, EC, N,P,K and organic matter measured.

The *p*H of the samples was measured in 1:2 soil water suspension with a *p*H meter with glass and calomel saturated electrode assembly. Electrical conductivity was measured with Philips conductivity meter with dip type cell at 30° ± 1° on the 1:2 soil water suspension. Organic matter was estimated as per Walkley and Black's method.[9] Available nitrogen was estimated as per alkaline $KMnO_4$ method.[10] Available phosphorous was determined colorimetrically by Olsen's method.[11] Available potassium was estimated turbiditimetrically[12] with turbidity measured by Bausch and Lomb spectronic '20' at 660 nm with a red filter.

Results and Discussion

The influencc of D-D mixture on organic matter, available N,P,K of a sodic saline soil is expressed in Table 1. Each reading in the table for individual doses represents a mean of seven values recorded at 0,15,30, 45, 60, 75 and 90 days after application of the fumigant. Similarly the average values for different days represent a mean of several values obtained at different doses viz., 0.0, 0.50, 1.00, 1.50, 2.00 and 2.50 ml per 2 kg soil. The results were subjected to statistical analysis and variance ratio, and LSD values were calculated using the value of t at 5% level of significance. In the discussion that follows, the average values for doses and days have been considered and the term significant is used as meaning statistically significant at 5% F level (2.52 for doses and 2.42 for days).

Effect on pH and EC: No significant changes in *p*H or electrical conductivity either with increase in doses of D-D mixture or with interval of time was observed in the fumigated samples.

Effect on organic matter : The data given in Table 1 showed a significant decline in organic matter content of the soil with increasing applications of D-D mixture. With passage of time, however, there was a significant rise upto 30 days and thereafter a continuous decline. The decline in organic matter can be explained by the fact that while fumigates like D-D greatly eliminate nematode population, many soil bacteria are fairly resistant to fumigants. The eradicant type chemicals produce greater re-invasion potentials[13] with the result that the reactivated soil organisms bring about a rapid decomposition of organic matter which significantly declines. Such effects have also been reported by Smith and Wenzel[14] as well as others in case of soils treated with chlorinated insecticides.

TABLE I—EFFECT OF D-D MIXTURE ON NUTRIENT AVAILABILITY FOR DIFFERENT DOSES OF THE MIXTURE AT VARIOUS INTERVALS OF TIME.

Applications : Doses (in ml per two kg of soil)/days	Average values of available nutrients for various doses and days in mg per 100 gm soil			
	Organic matter	Nitrogen	Phosphorous	Potassium
0.0	337.120	7.190	0.720	11.170
0.5	336.270	7.450	0.970	10.550
1.0	331.080	7.750	0.940	10.150
1.5	328.050	7.830	0.940	9.990
2.0	322.130	7.380	0.850	10.920
2.5	315.850	7.060	0.780	10.980
LSD	9.100	0.371	0 094	0.580
Variance ratio	9.407	7.819	9.660	7.849
0 days	294.120	2.800	0.600	5.250
15 days	335.060	8.710	0.950	10.720
30 days	358.530	9.420	1.120	13.410
45 days	354.970	8.550	1.030	13.170
60 days	328.080	7.880	0.790	10.810
75 days	316.650	7 550	0.740	11.010
90 days	311.699	7.180	0.680	10.020
LSD	8.320	0.340	0.086	0.530
Variance ratio	65.050	334.590	42.750	215.420

Effect on available nitrogen : Examination of the data given in Table 1 generally indicated increase in available nitrogen with increasing doses of D-D mixture upto a value of 1.5 ml per 2 kg of soil after which it declined. A significant rise also occurred with passage of time, reached a maximum at 30 days and thereafter declined. The initial increase in available nitrogen was due to the decomposition of soil organic matter by fumigant resistant bacteria[13] which resulted in the release of nitrogen. The decrease with large doses on the other hand appeared to be due to the inhibitory effects of large doses of fumigant of nitrification. The findings were in the agreement with the work of Walcott and co-workers[15] and Koike.[16] The decline with passage of time was due to the dissipation of the toxic chemical and reinfestation of high potential zones of the treated soil by the fast growing fungi of vigorously competitive sugar and amino acid utilising kinds. The results were in agreement with the findings of Kreutzer.[17]

Effect on available phosphorus : A reference to the results given in Table 1 generally indicated a significant increase in phosphorous availability upto 1.5 ml of D-D mixture per two kg of soil and upto 30 days of its application followed by a significant decline in both cases. Wensley[18] and Martin and co-workers[19] have reported increased and highly stimulated microbial activity in soil as a result of fumigation. The effects of reinfested fungus flora, ascomycetes and actinomycetes resulted in the decomposition of soil organic matter bringing about a gradual increase in phosphorous availability till a maxima was reached both with doses and passage of time. However, the toxic effect of too high doses, and certain chemical reactions like reduction of phosphorous to PH_3 with passage of time resulted in the decline of phosphorous.

Effect on available potassium : A reference to Table 1 revealed that potassium availability generally decreased with increasing application of D-D mixture upto 1.5 ml per 2 kg of soil and thereafter increased. With passage of time it increased upto 30 days and thereafter followed a fluctuating pattern. The mechanism by which the fluctuation occurred was not entirely clear. The suppressive influence on potassium availability in soil was probably the tendency of the fumigant to fix available potassium into non-exchangeable form on the clay lattice but further work is required to justify this conclusion.

Acknowledgement

The authors are grateful to Dr. Abrar Mustafa Khan, Professor of Botany, Aligarh Muslim University, for helpful suggestions.

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Spectrophotometric Studies on the Composition of Ammonia-Cobalt(II)-Dioxane Complex and its Application in the Estimation of Nitrogenas Kjeldahlised Ammonia

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Ammonia when allowed to interact with cobalt(II) in presence of dioxane produced a yellowish brown colour in the *p*H range 5.5–7.5. The colour proved to be sufficiently specific to warrant a close spectrophotometric examination as regards to proper wavelength, reaction ratio, the effect of time and other variables such as concentration of dioxane. The λ_{max} of the complex was found to be 390 nm and the reaction ratio by Job's method of continuous variation as 3 : 2. Results pointed to the possible application of this reaction for the spectrophotometric determination of Kjeldahlised nitrogen in soils and inorganic compounds.

A FEW methods for the determination of nitrogen are known. The most common of these methods is Kjeldahl's procedure[1] where nitrogen is estimated as ammonia. Nessler's Reagent[2,3,4] is sometimes used for the spectrophotometric determination of ammonia. Phenol hypochlorite[5,6] reagent is also used. A sensitive, selective and easy method for the determination of Kjeldahlised nitrogen will be of immense importance in the estimation of combined nitrogen in various important materials like soils, fertilizers, explosives and high polymers.

It was noticed in these laboratories that when an aqueous solution of ammonia was treated with an aqueous solution of cobaltous chloride, a green precipitate was produced. This precipitate when dissolved in dioxane yielded a yellowish brown colour. The colour reaction appeared to be sufficiently specific. Therefore it was considered worthwhile to subject it to a close spectrophotometric examination as regards to the nature of the complex formed and the possibility of its application in the spectrophotometric determination of nitrogen as Kjeldahlised ammonia in ammonium salts and soils.

Experimental

Apparatus : The absorbance measurements were made on Bausch and Lomb Spectronic '20' spectrophotometer. Pyrex glassware was used for the preparation of solutions and for carrying out the experiments. *p*H was measured with Beckman *p*H meter model G.

Reagents : Standard solutions of cobaltous chloride, ammonia and dioxane were freshly prepared by dissolving requisite weights of pure grade Merck's reagents in double distilled water.

Procedure and Results :

Spectral curves : Absorption spectra were recorded at 30°C and in the *p*H range 5·5 to 7·5. The method of Vosburgh and Cooper[7] was employed to ascertain the proper wavelength for carrying out spectrophotometric studies and to determine the number and nature of the complexes present in the colour. 0·005*M* solutions of cobalt and ammonia were mixed in the ratio 1 : 1, 1 : 2, 2 : 1, 4 : 1, 3 : 1 to 6 ml and to each of these 1·5 ml of 0·025*M* dioxane was added and the volume made up to 50 ml. Cobaltous chloride solution was used as a blank. The spectra showed a maxima at 390 nm (see Fig. 1, curves 1 to 4)

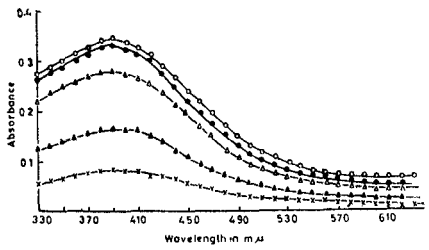

Fig. 1

in all cases, indicating that it was the most suitable wavelength for further spectrophotometric work. The results also pointed to the formation of only one complex in the above reaction.

Standard curve : A standard curve was drawn by distilling 0·02 g of NH_4Cl with 100 cc of 50% NaOH using Kjeldahl assembly and collecting the distillate in 25 ml of 0·1*M* Co(II) solution. Colour was then developed by adding 1·5 ml of 0·025*M* dioxane to various concentrations of the complex solution,

absorbance taken and a standard curve drawn. Beer Lambert Law was followed from 0 to 280 ppm of nitrogen by the above distillate mixture in the *p*H range of 5·5 to 7·5.

Effect of dioxane concentration : Concentration of dioxane was found to affect the colour intensity. Best results were obtained on adding 180 ppm of dioxane to the complex solution.

Full colour development occurred in about 30 min. The colour was stable for nearly 3 hrs. Thereafter precipitation occurred especially in the range of higher concentration.

Determination of reaction ratio : Job's method of continuous variation[8,9] was used to determine the composition of complex formed in the solution. For this purpose equimolar concentration of ammonia and cobaltous chloride were mixed and the requisite amount of dioxane added. The sum of the concentration of ammonia and cobalt(II) was kept constant viz., $2{\cdot}5\times10^{-4}M$, $2{\cdot}0\times10^{-4}M$ and $1{\cdot}66\times10^{-4}M$ respectively, while their ratio varied (see Fig. 2,

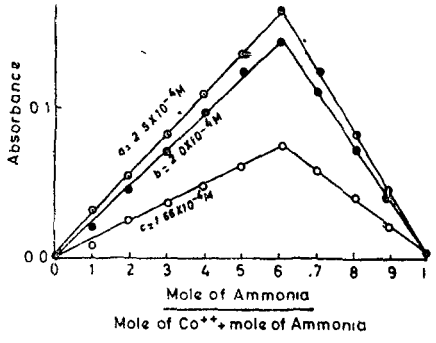

Fig 2

curves a, b and c). A plot of absorbance against mole ratio of ammonia for measurement at 390 nm gave maxima at a mole ratio of 0·6 in all cases pointing to the presence of a 3 : 2 complex of ammonia and cobalt, i.e.,

$$3NH_3 + 2Co^{2+} \rightarrow Co_2(NH_3)_3^{4+}$$

Determination of nitrogen as Kjeldahlised ammonia in ammonium salts : 0·02 g of each of NH_4Cl and $(NH_4)_2SO_4$ were distilled with 100 ml of 50% NaOH in Kjeldahl flasks and nitrogen estimated as ammonia with the help of the standard curve using cobaltous chloride and dioxane as colour reagents.

Nitrogen in soils : 1 g of soil, 10 g K_2SO_4, 0·5 g $CuSO_4.5H_2O$, a few pieces of porcelain and 25 ml of conc H_2SO_4 were taken in a Kjeldahl flask and shaken till the contents were well mixed. The mixture was digested till it became colourless (usually for 90-120 min). The flask was then cooled and 100 ml of water added. The mixture was distilled with 100 ml of 50% NaOH and a few fragments of granulated zinc. The distillate was collected in 25 ml of 0·1*M* $CoCl_2.6H_2O$ solution and the volume made to 500 ml. 5 ml of this solution was taken in a 50 ml flask and colour developed with 1·5 ml of 0·025*M* dioxane. After 30 min measurements were made on Bausch and Lomb spectronic "20" and the amount of nitrogen in soils calculated. Nitrogen was also determined as per usual Kjeldahl procedure. The results for amount of nitrogen obtained by the recommended method are given in Table 1.

Table 1. Percentage of nitrogen as estimated by different methods

Material used	Cobalt(II) dioxane method	Acid method	Theoretical value
NH_4Cl	24.76	24.62	24.34
$(NH_4)_2SO_4$	21.35	21.11	21.20
Soil Type 3	0.30	0.29	—
Soil Type 5	0 23	0.22	—

Discussion

An examination of the data obtained during the above investigations pointed to the definite possibility of the application of the colour reaction between ammonia, cobaltous chloride and dioxane for the detection and spectrophotometric estimation of Kjeldahlised ammonia in soils and in inorganic compounds. It is clear from table 1 that the results obtained by this method are almost of the same accuracy as the previous methods and can be successfully used for the determination of nitrogen in the case of soils and inorganic compounds. In the case of organic compounds, this method, however, failed to give satisfactory results.

Acknowledgement

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R E S U M E

The study of soils can provide interesting information in the fields of science, agriculture and engineering. The surface phenomenon, the physico-chemical and pesticidal aspects are of vital importance in modern crop production and environmental pollution. The subject offers many fascinating opportunities for a chemist to investigate. Techniques such as those of adsorption, ion exchange, chemical thermodynamics, chemical kinetics and plant nutrition can lead to interesting results in the study of clay and soil interactions.

Systematic studies in the above direction started in the later part of the current century when workers like Hendricks[1]; Mortland[2]; Swoboda and Kunze[3]; Weber et.al[4]; Bailey et al.[5]; Giles et al.[6]; Gaines and Thomas[7]; Deist and Talibudeen[8]; Jurinak and Bauer[9]; Singhal et al.[10-14]; Boyd et al.[15]; Dumal et al.[16]; Helfferich[17]; Vansant and Uytterhoeven[18] and Lindstorm et al.[19] established a definite link between clay chemistry and physical chemistry.

During the last decade, interest in the use of pesticides in crop disease and control vastly increased in India. One of the serious deficiencies in the successful and wide-spread use of pesticides was a non-developed application of proper doses in the different types of clay mineral containing soils. The pesticides are used as nematocides[20], herbicides, fungicides and insecticides. Organic molecules such as nicotine, D.D.T., Aldrin, thiocarbamate etc. find an important application as insecticides. Soil fumigants

such as methyl bromide, 1,3-dibromopropene, 1,2-dichloropropane and telone are widely used in the control of nematodes, root-rot fungi and weed growth.

On application to soils the pesticides may be adsorbed on the clay substrate, undergo an exchange with cations or anions of the clays, cause a variation in the nutrient availability and microorganisms of the soil and bring about various physico-chemical changes in the clays and soils. Adsorption of organic compounds on clay surfaces depends upon several factors[21,10], such as strong cation dipole attractions[21], hydrogen bonding, solvation of cations by polar molecules, coordination, cation exchange reactions, van der Waals interactions[22], pH and other environmental conditions.

Clay minerals constitute the most important reactive surfaces of the soil. They have been reported to provide heterogeneous chemical spots in the form of sorbed water around cations[3], hydroxyls at the edges, lattice surface oxygens and electrical double layer of changing polarity[23] at the edges. They possess electron accepting sites in form of exposed aluminium[24] and transition metals in higher valency state at the edges. The location[5] and distribution of exchange sites on clays is an important factor in the nature and extent of adsorption.

Clays occur widely as the colloidal constituent of soils. Inspite of their being the most reactive fraction of soils, relatively little data exist on the mechanism of interactions between the pesticides in solution and the surface phase of these minerals. Because of the existence of exchangeable cations at these interfaces

clay minerals on dispersion in solution exhibit an exchange potential and may form important exchangeable phases for some pesticides like nicotine, zinc compounds etc.

The effectiveness and availability of a pesticide in soil depends upon a large number of factors such as mechanism of adsorption on clay and soil surfaces, mechanism of exchange on clay and soil surfaces, soil microorganisms and pH, clay mineral composition etc.

The phenomena of adsorption and exchange increase the persistence[25] and check up the movement and degradation of pesticides. It also sometimes renders them inactive and may lead to physico-chemical changes[26] including nutrient availability to plants. There is some lack of information on soil pesticide interactions.

In view of the great importance of such effects in soils and clays, the widespread use of pesticidal chemicals and trace metals in modern crop production and the desirability of learning as much as possible concerning their behaviour in soils after their application it was considered that studies could be usefully undertaken on clay pesticide interactions with the help of exchange adsorption isotherms potentiometric studies, thermodynamic parameters, surface activity coefficients, chemical kinetics and physico-chemical and nutrient studies.

In the studies reported hereunder nicotine was selected as the organic pesticide for fundamental studies with clays. Zinc which is an important trace metal and whose compounds find important applications as pesticides was selected as the inorganic cation for

further fundamental investigations on clays. D-D mixture formed the organic chemical for applied investigations on two selected Indian soils. The interactions were examined from several angles and reaction mechanisms worked out with clays of diverse groups wherever necessary.

Soil fumigation is widely used in modern agricultural practice to obtain high yield of crops. Considerable work has been done in the field of nematode and fungus disease control with chloride and bromide containing fumigants[20,27] since around the first of the century. Workers[28,29] have reported varied physical, chemical and biological changes brought about by fumigants in soils. Work on the major nutrient availability in presence of pesticides has been reported by Freney[30], Castro[31], Wedding et al.[32], Alexander[33], Thiegs[34], Koike[35], Smith[36] and others[37]. Marked alterations in the activity and population of micro-organisms, accelaration and retardation in nitrification of ammonium nitrogen, increased availability of phosphorus and leachability of potassium are some of the reported results[38]. There have been variations in effects with lapse of time. Some of the conclusions drawn have been contradictory.

D.D. is a mixture of 1,2-dichloropropene and 1,3-dichropropene. It is an important nematocide and is extensively used for this purpose. The use of such chlorinated chemicals is finding increasing application in agriculture. Since it is possible that these pesticides may effect nutrient availability in soils and bring about other transformations, it is useful to examine the influence of this fumigant on nitrogen, phosphorus and potassium availability in a few selected

Indian soils. The effect of passage of time on some of these aspects is also worth examining. In view of the likely indiscriminate use of pesticidal chemicals in modern crop production, such studies can provide interesting results.

The subject matter of the thesis was investigated on the following lines:

(i) Adsorption of nicotine with hydrogen and sodium saturated dickites.

(ii) Adsorption and reactions of zinc with hydrogen and sodium saturated dickites.

(iii) Studies on the thermodynamics of exchange of nicotine with Al-montmorillonite.

(iv) Studies on the thermodynamics of zinc exchange with montmorillonite.

(v) Studies on the kinetics of zinc exchange with Na-dickite.

(vi) Studies on the influence of a pesticide (D-D mixture) on some nutrients of soils.

A brief account of the results achieved on the basis of the plan mentioned above is presented below:

ADSORPTION OF NICOTINE WITH DICKITES

In the first instance the adsorption of nicotine with hydrogen and sodium saturated dickites was examined. According to the results obtained the adsorption of nicotine on acid and base saturated dickites yielded cation dependent adsorption isotherms similar to class "H" and "L" respectively. The pH, electrical

conductivity changes and adsorption pointed to initial coordination of the nicotine molecule with H-dickite followed by interaction with the 'Lewis' acid sites at the edges. Adsorption of nicotine on Na-dickite, on the other hand, was weak and mainly due to hydrogen bonding followed by chemisorption at the edges. X-ray diffraction provided evidence that only edge sites were involved in the reaction.

ADSORPTION AND REACTIONS OF ZINC WITH HYDROGEN AND SODIUM SATURATED DICKITES

In this part of the study the effect of pH, time and temperature on the interaction of zinc with acid and base saturated dickites was investigated. Increase in pH resulted in an increase in adsorption of zinc in the higher concentration range. The adsorption increased rapidly and then slowly with increase in the time of interaction. The variation of rate constants and the half times of reaction suggested an exchange process controlled by film and possibly particle diffusion and thereafter fixation processes. The inferences found support from the nature of adsorption isotherms. Temperature affected adsorption with exothermic interactions. The activation energy of adsorption of zinc on Na-dickite was 14.0 KCal $mole^{-1}$.

STUDIES ON THE THERMODYNAMICS OF EXCHANGE OF NICOTINE WITH Al-MONTMORILLONITE

The interaction of nicotine on Al-montmorillonite was examined on the basis of Gaines and Thomas model of thermodynamic treatment in which the ion exchange equilibria involving the

interaction of nicotine with Al-montmorillonite was studied. The exchange isotherms, both at 30° and 60°C indicated a preference for aluminium ions by montmorillonite as compared to nicotinium ions. Separation factor supported the conclusion. Enthalpy gain was indicative of a tighter binding of aluminium. Entropy gain was indicative of a diffused and disordered arrangement of nicotinium ions in the Gouy layer with aluminium forming a more ordered arrangement in the Stern layer.

STUDIES ON THE THERMODYNAMICS OF ZINC EXCHANGE WITH MONTMORILLONITE

In this part of the study the ion exchange equilibria and mechanism of zinc exchange with sodium montmorillonite was studied with the help of adsorption isotherms and thermodynamic parameters. The exchange isotherms, K and ΔG° values indicated a spontaneity of reaction and a higher preference of zinc for the montmorillonite surface. A stronger binding of zinc and changes in the hydration rates of zinc and sodium with increase in order was suggested by enthalpy and entropy effects respectively. The surface phase activity coefficients and the excess thermodynamic functions were indicative of a nonideal heterogeneous exchange in which the mixture of zinc and sodium ions on the montmorillonite surface was more stable and more tightly bound with significant differences in the hydration rates of the ions in the mixture with respect to the homo-ionic forms.

STUDIES ON THE KINETICS OF ZINC EXCHANGE WITH Na-DICKITE

A kinetic approach to ion exchange equilibria involving

inorganic ions on clays has recently gained considerable importance. Investigations in this chapter are based on Boyd, Adamson and Myers model in which a kinetic study was made to predict the behaviour of zinc exchange over sodium dickite. The rate determining step as revealed by the interruption and equation tests for the zinc exchange over Na-dickite was film diffusion at all the dilutions and temperatures investigated. Diffusion coefficients, half times of exchange, energies of activation and other kinetic parameters were calculated and used to predict the theoretical behaviour of the exchange.

STUDIES ON THE INFLUENCE OF A PESTICIDE (D-D MIXTURE) ON SOME NUTRIENTS OF SOILS

Lastly the results of fumigation of a mixture of dichloropropane and dichloropropene on the physico-chemical characteristics and major nutrients of a black cotton soil and a saline soil were studied. In the case of black cotton soil the results of statistical analysis of the experimental data showed that while in smaller doses the fumigant significantly stimulated the availability of nitrogen and phosphorus higher doses tended to be toxic. Lower doses had a non-significant suppressive influence on potassium availability. Organic matter was significantly reduced with increasing doses of D-D mixture. In general the stimulation after reaching a maximum gradually declined. There was no marked effect on the pH and electrical conductivity. The results were explained on the basis of microbial activity. In the case of the saline sodic soil, the results were almost similar. The two diverse soils thus behaved almost similarly towards D-D mixture fumigati

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